

T_g is approximately -40 to -42°C

Unexpectedly, the resulting coprepolymer sequence of this invention is random. The random sequence of the coprepolymer, together with the presence of the assymetric FOX segment, results in a low viscosity oil which significantly facilitates processing and the commercial application of the product.

The surface energy of the FOX/THF coprepolymer as a cured polymer is lower than that of polytetrafluoroethylene (Teflon) and is attributed to the presence of the fluorine in the side-chains rather than the backbone. It is noteworthy that the FOX/THF prepolymer is formed from the mono-substituted FOX monomers of this invention and the surface energy is comparable to that of the polymers formed from the bis-substituted monomers described in the background. Consequently, the FOX monomer is preferable to the bis-perfluoroalkyl monomers of the background, not only because the mono-substituted FOX monomers produce products having comparable or better surface energy, but also because of its ability to copolymerize with THF, thus reducing the starting materials cost. Even though we have significantly reduced the amount of fluorine in the FOX/THF coprepolymer by introduction of the THF segments, no significant reduction in surface energy is observed as compared to the polymers prepared from the mono-substituted FOX monomers.

The random nature of the co-prepolymer sequence is wholly unexpected and is achieved with the novel reaction conditions outlined below. The randomness results in an amorphous, low viscosity oil. The benefits of a liquid prepolymer over a crystalline prepolymer (as would be expected for a block copolymer or a prepolymer produced from a bis-substituted monomer) include easier processing and mixing with reactants (e.g., diisocyanates, cross-linkers, chain extenders, etc.).

The method of making the co-prepolymer includes the steps of:

- 1) premixing THF in an appropriate organic solvent, said THF and solvent temperature between -20°C and +60°C;
- 2) adding a catalyst;

- 3) adding an initiator;
- 4) adding a FOX monomer(s); said FOX monomer(s) temperature between -20°C and $+60^{\circ}\text{C}$;
- 5) quenching the reaction; and
- 6) separating the FOX/THF prepolymer by precipitation in methanol.

Alternately, where the copolymer ratio of FOX to THF is between the range of 60:40 and 35:65, no organic solvent is required and the prepolymer may be made by addition of FOX to neat THF. The absence of solvent offers significant advantages to manufacturers with respect to the environmental costs associated with solvent hazardous wastes and hazardous materials storage and handling, as well as the lower manufacturing costs and enhanced public perception (i.e., a "green" product). Further, the presence of the hydrocarbon segment (the THF segment), improves solubility of the co-prepolymer in hydrocarbons.

The copolymerization is conducted either in an inert solvent like methylene chloride or Freon 113 or mixtures thereof, or in neat THF. The 90:10 7-FOX/THF co-prepolymer is prepared in a 3:1 mixture of methylene chloride and Freon 113, whereas the 60:40 and 35:65 7-FOX/THF co-prepolymers are prepared in neat THF. Similarly, 50:50 13-FOX/THF and 60:40 15-FOX/THF co-prepolymers are prepared in neat THF. In the synthesis of 90:10 7-FOX/THF co-prepolymer, solvent is used to avoid viscosity build-up during polymerization, and can potentially be eliminated by using high torque mixers. Solution polymerization may be conducted at a solids concentration of 5%-85%, however, polymerization is normally conducted at a concentration of 50-60% solids. Other solvents that can be used for this process are carbon tetrachloride, chloroform, trichloroethylene,

chlorobenzene, ethyl bromide, dichloroethane, fluorinated solvents, sulfur dioxide, hexanes, petroleum ether, toluene, dioxane, xylene, etc. with the preferred solvent being methylene chloride, or a mixture of methylene chloride and Freon. The fact that FOX/THF copolymers can be prepared in the absence of a solvent is beneficial in the view of full scale production, since environmental regulations highly restrict the emission of solvents, specially halogenated solvents, into the atmosphere.

The catalyst and the initiator are similar to those used in the homo-polymerization of FOX monomers. Suitable catalysts are Lewis acids i.e., compounds capable of accepting a pair of electrons, example of which include: complexes of boron trifluoride, phosphorous pentafluoride, SnCl_4 , antimony pentafluoride, etc. Suitable initiators are water and aliphatic alcohols containing 2 to 5 carbons and 1 to 4 hydroxy groups, e.g., trifluoroethanol, methanol, 1,4-butanediol, trimethylolpropane, pentaerythritol, etc.

In a typical example, the catalyst and the initiator are mixed in a solvent prior to the addition of the monomer. THF is a five membered cyclic ether with low strain energy, and does not homopolymerize under the reaction conditions. Thus, THF is added in one shot to the reaction mixture. On the other hand, oxetane monomers possess relatively high strain energy and undergo exothermic, ring-opening polymerizations. Thus, FOX monomers are added slowly over a period of time to control the reaction temperature and to avoid run-away reactions. The progress of the reaction is monitored by ^1H NMR and when >95% of FOX monomer is

consumed, the reaction is quenched with water. The prepolymer is purified by precipitation in methanol.

The molecular weight of the co-prepolymer can be controlled by varying the monomer/catalyst ratio and the reaction temperature. Generally, lower monomer/catalyst ratios and higher reaction

temperatures favor the formation of lower molecular weight co-prepolymers. The ratio of monomer to catalyst can be from 10:1 to 300:1, however, the ratios commonly used are 100:1 monomer/ catalyst. The temperature can be from -20°C to +60°C, however, the preferred reaction temperature is +5°C. At higher temperatures, formation of monofunctional materials, mainly -CH₂F terminated materials, is observed. The +5°C mean reaction temperature eliminates the formation of -CH₂F terminal groups which are unreactive and would otherwise reduce the functionality of the prepolymer (by formation of the mono-functional product) and lead to polyurethanes with poor mechanical properties.

In contrast to the FOX homo- and co-prepolymers, the formation of cyclic oligomers is not observed in the copolymerization of 7-FOX with >10 % mole THF. Similarly, formation of cyclic oligomers is not observed in the preparation of 50:50 13-FOX/THF and 60:40 15-FOX/THF co-prepolymers. A small amount of cyclic tetramer (ca. 1.0%), however, is formed in synthesis of 90:10 FOX/THF co-prepolymer. It is postulated that incorporation of THF in the growing polymer chain changes the number of atoms in the polymer chain and does not allow the chain to bite back and form a thermodynamically stable, 16-membered cyclic ether. This result is

especially important in the development of non-toxic fouling release coatings, where discharge of any chemicals from candidate coatings is not acceptable.

5 The FOX/THF co-prepolymers of this invention are amorphous, low viscosity oils that are easy to process. FOX/THF co-prepolymers are slightly more viscous than FOX homo-prepolymers. The inherent viscosity of a 60:40 7-FOX THF co-prepolymer, determined in THF at 0.5 g/dL concentration, is 0.125 dL/g. By comparison, the inherent viscosity of the 7-FOX homo-prepolymer is 0.072 dL/g. ¹H NMR analysis
10 of FOX/THF co-prepolymers indicates that both monomers are incorporated into the co-prepolymer, and that the THF segment is present in the middle of two FOX segments, and not as an end group.

The ratio of the two monomers in the co-prepolymer is established by comparing the area under the peaks corresponding to
15 THF (ca. 1.6 ppm) and 7-FOX (0.93 ppm) segments. ¹H NMR analysis also indicates that FOX/THF copolymers are not contaminated with monofunctional materials (-CH₂F terminated) or other impurities. Presence of multiple peaks in the quaternary carbon region of ¹³C NMR, corresponding to the carbon bearing the fluoroalkyl side-chain,
20 reveal that the above prepolymers are random copolymers with little, if any, block structure. ¹⁹F NMR analysis confirm the presence of the fluoroalkyl side-chain and the absence of -CH₂F end groups, HF and BF₃ catalyst. It is important to note that these materials are not block copolymers, since THF blocks could crystallize and lead to
25 materials with increased crystallinity and poor flexibility. This, in turn, would limit the usefulness of FOX/THF materials.

The number average molecular weights of FOX/THF co-prepolymers, as determined by GPC, were between 10,000 and 14,000, whereas polydispersities were between 1.5 and 2.1. The co-prepolymers exhibited unimodal molecular weight distribution, and with the exception of 90:10 7-FOX/THF co-prepolymer, FOX/THF co-prepolymers were free of cyclic oligomers. The equivalent weight of 60:40 7-FOX/THF co-prepolymer, determined by ^1H NMR employing TFAA end group analysis, was 6,230. The equivalent weight of the same co-prepolymer by p-toluenesulfonyl isocyanate/ dibutyl amine titration method was 5,890. The glass transition temperature of the 60:40 7-FOX/THF co-prepolymer by DSC analysis was -43°C ; no other transitions were detected between -100°C and $+130^\circ\text{C}$. By comparison, the glass transition temperature of the 7-FOX homo-prepolymer was -42°C . This result indicates that the glass transition temperature of the co-prepolymer is not affected by the incorporation of THF, and that the prepolymer is a random copolymer. If the prepolymer was a block copolymer or a mixture of two homopolymers, more than one transition would be observed. This was further confirmed by the dynamic mechanical property measurements of 60:40 7-FOX/THF co-prepolymer where only one transition (T_g) was observed at -41°C . It should be noted that the formation of a random copolymer between FOX and THF monomers is unexpected since the vast difference in the reactivity of these two monomers would dictate the formation of a block copolymer or two homopolymers.

The co-prepolymers described above are oils that can be used

as lubricants or as additives for a variety of applications. For example, the co-prepolymers can be used as additives to improve the performance of commercial engine oils or as a lubricant for industrial equipment. The major use of FOX/ THF co-prepolymers, however, is in the development of fluorinated polyether urethane elastomers.

3. Polymers

The hydroxy terminated prepolymers of this invention can be used for the synthesis of a variety of polymers such as polyurethanes, polyesters, polycarbonates, polyacrylates, etc. Additionally, the FOX prepolymers of this invention may be used to synthesize novel fluorinated elastomers, thermosets and thermoplastics.

The fluorinated polyurethane elastomers of this invention exhibit the surface properties of fluoropolymers, and the mechanical properties and the processing characteristics of traditional polyurethanes. These materials exhibit low glass transition temperatures, low coefficient of friction, high abrasion resistance, and extremely low surface energies. In addition, these polymers exhibit excellent mechanical properties and can be processed as thin coatings or into bulk articles. Also fluorinated polyurethane of this invention can be bonded to a variety of substrates. Combination of these properties, make these materials attractive for a variety of applications such as fouling release coatings for ship hulls and other marine structures; drag reducing coatings for ship hulls and aircraft; moisture barrier coatings and encapsulants for electrical

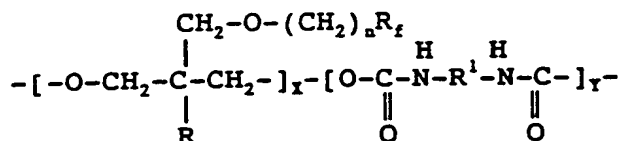
circuits; ice release coatings for aircraft and structures; anti-corrosion and protective coatings; coatings for automotive top coats (e.g., car wax), gaskets and seals; backing for adhesive tape; windshield, eyeglass, and window coatings; binders for propellants and flares; bushings for vibration damping; furniture polish; non-transferable, water/oil proof cosmetics; water repellant for fabrics; oil/stain resistant coating for carpets; low friction coating for computer disks and magnetic head rails; and numerous medical/dental applications such as artificial hearts, artificial joints, catheters, contact lenses and intraocular lenses.

Polyurethanes from FOX Homo-/Co- Prepolymers

The preparation of fluorinated polyurethane elastomers begin with the FOX prepolymers of this invention. As previously described, these prepolymers are amorphous, low viscosity oils that are easy to process. Moreover, these materials are difunctional and possess terminal primary hydroxy groups that react readily with isocyanates to form high molecular weight polyurethane elastomers. Typically, the prepolymer is reacted with an equivalent amount of a polyisocyanate in the presence of a catalyst and a crosslinking agent to form a three-dimensional, polymer network. The process involves mixing the components, casting them in a mold, degassing, and curing the mixture at an elevated temperature. Alternately, the FOX prepolymer is reacted with excess diisocyanate and the resulting isocyanate-capped prepolymer is reacted with the crosslinking agent to form the thermoset. If desired, the isocyanate capped-prepolymer

can be reacted with a low molecular weight diol or diamine (a chain extender) to form a linear, thermoplastic polyurethane elastomer.

The fluorine-containing thermoset polyurethane elastomer of this invention is composed of repeat units, bounded by cross-linking agents, which have the following structure:



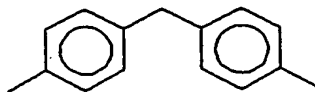
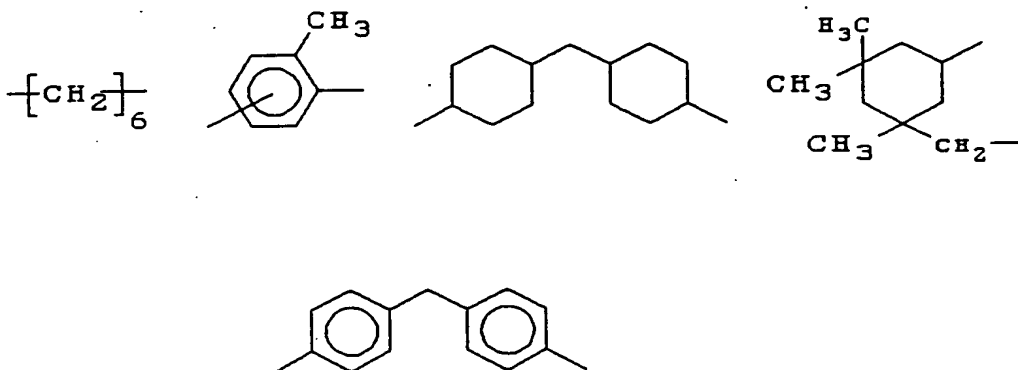
where: n is 1-3;

R is methyl or ethyl;

R_f is a linear or branched perfluorinated alkyl group having 1-20 carbons, or an oxaperfluorinated polyether having from about 4-20 carbons

X is 10-200 and Y is 1-10

R¹ is an alkyl or aryl functional group, examples of which include the following structures:



The resulting polyurethane is tack-free, opaque, generally insoluble in organic solvents and has a glass transition temperature

between -40°C and -47°C. Contact angle measurements of between 110° and 145° with distilled water and surface energy measurements of 13.8 - 15.2 ergs/cm² indicate that the surface wettability (hydrophobicity) and non-adhesive characteristics of the elastomer of this invention are greater than those measured for Teflon (110° contact angle and 18.5 ergs/cm² surface energy). We have observed that as the size of the side-chain on the FOX polymers increases, hydrophobicity increases as well (see Table 3). As indicated above, the 145° contact angle of the polyurethane derived from the 15-FOX prepolymer is characteristic of the extreme hydrophobicity of the FOX polymers of this invention. The 145° contact angle of the 15-FOX polyurethane is one of the highest ever observed.

Figure 1 shows the contact angle of a drop of doubly distilled water on the 15-FOX polyurethane of this invention as compared to the contact angle of a doubly distilled drop of water on Teflon.

The polyurethanes of this invention exhibit the following novel set of characteristics:

- 1) Elastomeric properties;
- 2) More hydrophobic and non-stick than Teflon;
- 3) Processable into thin coatings or bulk articles;
- 4) Flexible down to about -50°C ;
- 5) Bondable to a variety of substrates; and
- 6) Useful ambient temperature range from about -50°C to about 240°C.

Glass transition temperature is the temperature at which the polymer is transformed from a brittle glass to a flexible elastomer. Thus, it dictates the lower use temperature of the elastomer. The glass transition temperatures of non-plasticized FOX polyurethanes, as measured with a differential scanning calorimeter (DSC), are between -40°C and -47°C. Normally, a plasticizer is used to impart flexibility and to lower the glass transition temperature of polymers. If desired fluorinated plasticizers such as Fomblin, Alfunox, and Kel-F oils can be used to improve the low temperature

flexibility of FOX polyurethane elastomers.

Contact angle is the obtuse angle of a water droplet on the polymer surface and reflects the wettability of the polymer surface. A water droplet does not spread on a hydrophobic surface and will exhibit a high contact angle, indicating non-wetting characteristics of the polymer surface. The static contact angle of FOX polyurethanes with doubly distilled water were measured with a Goniometer, and were found to be between 110° and 145° . In sharp contrast, Teflon exhibits a contact angle of 110° . Surface energy is also an important measure of wettability of the polymer surface and defines critical properties such as its hydrophobicity and adhesive characteristics. Materials with low surface energies are difficult to wet and thus exhibit excellent release characteristics. Teflon, for example, exhibits a surface energy of 18.5 ergs/cm^2 , and is widely used in preparation of non-stick cooking utensils. Surface energies of common polymers are listed in Table 2. The surface energies of polyurethanes prepared from Poly 3/7 FOX (25:75) and Poly 7-FOX are 15.2 and 13.8 ergs/cm^2 , respectively. These values are considerably lower than that of Teflon and other commercial polymers, indicating that FOX polyurethanes have superior release characteristics to Teflon. This makes the cured elastomer of this invention more suited than Teflon for those applications where lower wettability and enhanced released characteristics are desired in a coating material.

TABLE 2
SURFACE ENERGIES OF COMMERCIAL POLYMERS

MATERIAL	SURFACE ENERGY (ERGS/CM ²)
Teflon	18.5
Polydimethylsilanes	24
Polyethylene	31
Polytrichlorofluoroethylene	31
Polystyrene	33-35
Poly(methyl-methacrylate)	33-34
Nylon 66	46

The method of making the polyurethane elastomer includes the steps of:

- 1) Premixing a FOX prepolymer with a polyisocyanate at a reagent temperature between 25°C and 100°C;
- 2) Adding a catalyst;
- 3) Adding from about 0% to 15% wt/wt of a cross-linking agent;
- 4) Mixing the components;
- 5) Casting the components into a mold;
- 6) De-gassing the cast compound; and
- 7) Curing the compound mixture at a temperature of between 17°C and 150°C.

Normally, molar equivalent amounts of FOX prepolymer, cross-linking agent and polyisocyanate are used. However, where the FOX prepolymer is added to an excess of polyisocyanate, an isocyanate-capped prepolymer is produced which may be further reacted with a cross-linking agent to produce a thermoset polyurethane elastomer. Alternately, the isocyanate-capped prepolymer can be reacted with a low molecular weight chain extender such as a diol or diamine to

prepare linear thermoplastic polyurethane elastomers.

The crosslinking agents normally used are low molecular weight polyols or polyamines such as trimethylolpropane, pentaerythritol, Isonol 93, trimethylolethane, triethanolamine, Jeffamines, 1,4-butanediamine, xylene diamine, diethylenetriamine, methylene dianiline, diethanolamine, etc. The preferred crosslinking agents are trimethylolpropane, Isonol 93, methylene dianiline, and Jeffamines. The mechanical properties of an elastomer can be altered by varying the amount of crosslinking agent. Generally, increasing the amount of crosslinking agent in a polyurethane formulation leads to materials with higher modulus and improved chemical and abrasion resistance. The amount of crosslinking agent can be varied from 0-15% by weight, however, the preferred amount is between 1.5% and 5% by weight.

The preferred catalyst is dibutyltin dilaurate, however, a variety of catalysts such as triethyl amine, triethylene diamine, triphenyl bismuth, chromium acetylacetonate, lead octonate, ferric acetylacetonate, tin octanoate, etc, can also be used. It should be noted that the catalyst is added primarily to increase the rate of the reaction, and if desired the reaction can be conducted in the absence of the catalyst. The catalyst concentration can be between 0.001 to 1% by wt., however the preferred concentration is between 0.1% and 0.2% by wt.

The polyisocyanates useful in the synthesis of FOX polyurethanes are: hexamethylene diisocyanate (HDI), Isophorone diisocyanate (IPDI), Methylene diphenylisocyanate (MDI), saturated MDI (Des-W), polymeric MDI (Isonates), toluene diisocyanate (TDI), polymeric HDI (N-100 and N-3200), cyclohexylene-1,4-diisocyanate, and 2,2,4-trimethylhexamethylene diisocyanate. The NCO:OH ratio can be from 1.1 to 0.9, however the preferred ratio is 1.02.

Bulk materials are prepared by casting the above formulation in a mold, degassing the mixture, and then curing it at 65°C for 16 to 36 h. A thin film is prepared by diluting the above formulation with THF, spreading the mixture over the substrate with a Doctor's

blade, and then curing the coated substrate in an oven at 65°C. Alternately, the substrate can be dip-coated or spray coated and cured in an oven at 65°C.

The cure temperature can be between 20°C to 150°C. The preferred temperature is 65°C. The above formulation can be cured at room temperature by increasing the amount of catalyst to ca. 0.5%. The cure is also dependent on the thickness of the sample and type of crosslinking agent. Thin samples cure within 3 h at 65°C, whereas 1/8 inch thick sample take between 8-16 h to cure. Also, amine-based crosslinking agents promote faster cures than polyols.

The mechanical properties of an unfilled elastomer are shown in Table 3. These properties indicate that polyurethanes prepared from FOX prepolymers are true elastomers (i.e., >100% recoverable elongation).

TABLE 3

No.	Prepolymer	%F	Contact Angle	Tensile Modulus	Strain	Stress	Water Abs.
1	Poly 3-FOX	31	110°	79	926%	670	---
2	Poly 3/7-FOX (25:75)	43	114°	34	1,256	427	0.22%
3	Poly 7-FOX	47	119°	41	1,308	622	0.16%
4	Poly 3/15-FOX (25:75)	52	128°	67	1,117	344	0.18%
5	Teflon	76	112°	---	---	---	---

The effect of a filler on mechanical properties is demonstrated in Table 4.

TABLE 4

No	FILLER		Contact Angle	MECHANICAL		
	Type	%		T.Mod	Strain	Stress
1*	---	0	114°	34 psi	1,256 %	427 psi
2	Teflon	5	---	41 psi	1,616 %	556 psi
3	Teflon	10	---	53 psi	1,294 %	500 psi
4	Teflon	20	---	73 psi	1,226 %	425 psi
5	Carbon Black	0.25	108°	42 psi	1,605 %	444 psi

* Base polymer: Polyurethane from 25:75 Poly 3/7-FOX

As expected, the tensile modulus increases and % elongation decreases with increasing filler loading. It is noteworthy that the use of a low energy filler like Teflon does not degrade the mechanical properties of FOX polyurethane elastomers. This indicates that FOX polyurethanes will wet Teflon and thus allow Teflon to disperse, rather than agglomerate, in the filled polymer.

Surprisingly, FOX polyurethanes exhibit good adhesion to a variety of substrates such as stainless steel, aluminum, graphite, EPDM rubber, glass and wood. In a typical process, the substrate is coated with the polyurethane formulation, placed in an oven, and cured. Please note that no special treatment or primer is required to bond fluorinated polyurethane to the substrate. Peel strength indicates the bonding characteristics of the coating to substrate and is measured with an Instron. Polyurethanes from hydroxy-terminated polybutadiene bond strongly to EPDM substrates and exhibit peel strengths that are in the neighborhood of 9.5 lbs/in; the bond failure is cohesive. The polyurethane prepared from FOX-7 prepolymer, Isonol-93, and Des-W exhibit a peel strength of 9.5 lbs/in and an adhesive bond failure. The good bonding characteristics of FOX polyurethanes is attributed to the presence of

polar urethane groups in the polymer backbone, which in contrast to fluoroalkyl groups, orient towards the high energy surface. A well adhering coating should, therefore, contain chemical groups that will contribute to enhance the polarity of the coating and bring it into the range of the substrate. A system containing both dipole-dipole and hydrogen-bond contributions is preferred over a system containing only one such contribution because of its broader compatibility. During application, the system must be sufficiently fluid in order to encourage rapid spreading, uniform coating and good wetting. Since Teflon has the fluorine symmetrically bonded to the polymer backbone, there is no dipole or hydrogen bonding with which the polymer may bond to a substrate surface. Consequently, a Teflon coating will not exhibit good adhesion or peel strength with its underlying substrate.

Thermal stability of FOX polyurethanes was determined by thermogravimetric analysis (TGA). These materials exhibit 0% wt. loss in air to 260 °C and onset of major thermal degradation in air at 275°C. This study indicates that FOX polyurethanes should not be exposed to temperatures in excess of 250°C.

The above results indicate that the polyurethanes prepared from FOX prepolymers are more hydrophobic and non-stick than Teflon. In sharp contrast to Teflon, FOX polyurethanes are tough elastomers that can be processed into thin coatings or into bulk articles. Moreover, these materials are flexible at low temperatures and can be used at temperatures as low as -50°C. Also, these materials can be bonded to a variety of substrates, and can be used between the temperature limits of -50°C and 250°C. This invention provides novel materials that can be bonded strongly to a variety of substrates and at the same time provide a surface that is more hydrophobic and non-stick than Teflon. Materials with combinations of these properties are not known and thus FOX polyurethanes fulfill an important niche in the market place for processable, low surface energy elastomers.

Polyurethanes From FOX/THF Co-prepolymers

FOX/THF co-prepolymers may be also used to produce polyurethane elastomers with useful properties. Polyurethanes prepared from FOX/THF co-prepolymers exhibit better adhesion, higher abrasion resistance, and superior mechanical properties than those derived from FOX homo-prepolymers. Moreover, the key properties of FOX polyurethanes are not affected by incorporation of THF in the polymer structure. That is, polyurethanes prepared from FOX/THF co-prepolymers still exhibit low glass transition temperature, low coefficient of friction, and low surface energy--properties that are similar to those of polyurethanes derived from FOX homo-prepolymers.

The FOX/THF co-prepolymers described in this invention are difunctional and have terminal hydroxy groups. These hydroxy groups are primary and react readily with isocyanates to form high molecular weight polyurethane elastomers. In a typical reaction, the co-prepolymer is reacted with an equivalent amount of polyisocyanate in the presence of a catalyst and a crosslinking agent to form a 3-dimensional polymer network. If the functionality of the polyisocyanate is 2, then a crosslinking agent is needed to form a crosslinked network. However, if the functionality of the polyisocyanate is >2 , then no crosslinking agent is needed. In some cases, additional crosslinking agent is added to improve the chemical and abrasion resistance of the polymer. The crosslinking agent normally used is a low molecular weight polyol or polyamine such as trimethylolpropane, Isonol 93, Jeffamines, trimethylolethane, pentarerythritol, triethanol-amine, diethanolamine, 4,4-methylene dianiline, MOCA, 1,4-butanediamine, diethylenetriamine, xylene diamine, etc. The preferred crosslinking agents are Isonol 93, trimethylolpropane and Jeffamines. The preferred catalyst is dibutyltin dilaurate, however other catalysts such as triethylamine, DABCO, Ferric acetylacetonate, triphenyl bismuth, tin octanoate, lead octanoate, etc., can also be used. The catalyst concentration is normally between 0.1 and 0.2% by weight. The polyisocyanates useful in the synthesis of fluorinated polyurethanes are hexamethylene diisocyanate (HDI), Isopherone diisocyanate (IPDI), 4,4-methylene

diphenylisocyanate (MDI), polymeric MDI (Isonates), toluene diisocyanates, saturated MDI (HMDI), polymeric HDI (N-100 and N-3200), and trimethylhexane diisocyanate. The NCO:OH ratio can be from 1.1 to 0.9, but the preferred ratio is 1.02. Bulk materials are prepared by casting the above formulation in a mold, degassing the mixture under reduced pressure for 15 mins, and then curing it in an oven at 65°C for 16 h. If a thin film is desired, a solvent, like THF, is added to reduce the viscosity, and the mixture is spread over the substrate with a doctor's blade to form a film of desired thickness. Alternately, the substrate can be dip-coated or spray coated, then cured in an oven at 60°C - 65°C.

Cure, that is the reaction of prepolymers with polyisocyanates and crosslinking agents to form high molecular weight, crosslinked polymer network, is normally conducted at temperatures from 20°C to 150°C. The preferred cure temperature is 65°C. The above formulations can be cured at room temperature by increasing the amount of catalyst to 0.5%. Also, thin films cure faster than bulk materials. The cure time is also dependent on the amount of the catalyst, temperature, and the type of crosslinking agent. Higher catalyst loading and higher temperature favor faster cures. Also, amine-based cross-linking agents promote faster cures than polyols. A formulation containing FOX/THF co-prepolymer, Isonol-93, HMDI, and 0.2% wt. catalyst cures in ca. 7 h at 65°C to give a tack free, 1/8 inch thick polyurethane elastomer. Under similar conditions, a 20 mil thick film will cure in 2 h at 65°C. When the above cure is repeated with an amine crosslinking agent, the cure time is reduced to <30 mins at 40°C.

In general, polyurethanes prepared from FOX/THF co-prepolymers are tack-free, opaque elastomers. They exhibit glass transition temperatures between -41°C and -46°C, and static contact angles with water between 108° and 126°. These materials are insoluble in common organic solvents like methanol, toluene, hexanes, carbon tetrachloride, methyl ethylketone and kerosene, but swell in

THF and Freon 113. The mechanical properties of an unfilled elastomer, as measured with an Instron, fall within the following limits:

5 Tensile Modulus: 35 psi to 205 psi
Elongation at Break : 400% to 1624%
10 Tensile Strength: 380 psi to 624 psi

10 An elastomer that has been characterized in detail is prepared from 60:40 7-FOX/THF co-prepolymer, Isonol 93 and HMDI, in the presence of dibutyltin dilaurate catalyst. The candidate material, a 3 x 5 x 0.2 inch³ sample, is an opaque elastomer. The static contact angle of this material with doubly distilled water is 117°. By comparison, static contact angles of water with Teflon and 7-FOX polyurethane are 110° and 119°, respectively. The surface energy of the candidate material, as determined by the method of Wu et al., is 13.5 erg/cm². This value is considerably lower than that of Teflon (18.5 ergs/cm²), but similar to that of 7-FOX polyurethane (13.2 ergs/cm²). The above results indicate that polyurethane prepared from 7-FOX/THF co-prepolymer is comparable in release characteristics and hydrophobicity to 7-FOX polyurethane, but is substantially more hydrophobic and non-stick than Teflon. In view of the reduced amount of fluorinated starting materials required to assemble the mono-substituted FOX monomers of this invention and further in view of the reduced amount of FOX monomer required in order to assemble a FOX/THF co-prepolymer, there is a significant cost savings over prepolymers assembled from the bis-substituted monomers or prepolymers assembled solely from the FOX monomers.

The candidate material exhibits a tensile modulus of 53 psi, elongation at break of 1624%, and a tensile strength of 624 psi. Recoverable elongation is in the neighborhood of 1200%. By comparison the mechanical properties of 7-FOX polyurethane are:

5 tensile modulus = 41 psi; elongation at break = 1308%; and tensile strength = 622 psi. This result is particularly interesting since it indicates that copolymerization of 7-FOX with THF improves both stress and strain capabilities of the 7-FOX polyurethane elastomer.

It should be noted that the mechanical properties can be tailored by varying factors such as, crosslink density, type of isocyanate, amount of plasticizer, filler loading, % hard block, etc. The glass transition temperature of the elastomer, as measured with DSC, was -43°C, whereas by rheometric mechanical spectrometer (RMS) it is -42°C.

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The candidate material exhibits good to excellent adhesion to a variety of substrates such as, stainless steel (SS 304), graphite, EPDM rubber, aluminum, and glass. Typically, the substrate is cleaned with water and acetone and then dried in an oven prior to use. Bonding is achieved by curing the mixture of prepolymer, cross-linking agent, polyisocyanate, and the catalyst directly on the substrate.

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In one experiment, EPDM substrate was coated with a 0.20 inch thick film of the candidate material, and peel strength was measured with an Instron. The candidate material exhibited a peel strength of >10 lb/in with a cohesive bond failure. The peel strength of 7-FOX/THF polyurethane compares favorably with the peel strength of polyurethane prepared from hydroxy-terminated

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polybutadiene, Isonol 93 and HMDI (>9.8 lb/in, cohesive failure). The peel strength of 7-FOX polyurethane on EPDM rubber was 9.5 lbs and the failure was adhesive. Ideally, high peel strength characterized by cohesive failure is desired (i.e., the material will
5 tear before delaminating from the substrate).

The coefficient of dynamic friction is approximately 0.33 for 7-FOX/THF polyurethanes and 0.31 for 7-FOX polyurethanes. By comparison, the coefficient of dynamic friction for a typical non-fluorinated polyurethane coating containing silicon oil is
10 approximately 0.95.

The above results indicate that the copolymerization of FOX monomers with THF not only reduces the cost of manufacturing fluorinated prepolymers, but also provides material with superior
15 properties. Moreover, FOX/THF polyurethanes exhibit better adhesion and superior mechanical properties than FOX polyurethanes, while retaining the key properties of FOX polyurethanes such as low glass transition temperature, high adhesion, processibility, high hydrophobicity, low coefficient of friction, and low surface energy.

Due to their unique combination of properties, polyurethanes prepared from FOX/THF co-prepolymers are useful as: fouling release coatings; abrasion resistant, low friction coatings for glass run
20 window channels, belts and windshield wipers; bushing, gaskets, and engine mounts; encapsulants for electronic devices; binders for propellants and flares; artificial joints; dental materials; and
25 coatings for automotive, marine and industrial applications. The preferred applications are fouling release coatings, coatings for

window channels,, and binders for propellants and flares.

DETAILED DESCRIPTION OF THE BEST MODE

5 The following detailed description illustrates the invention
by way of example, not by way of limitation of the principles of the
invention. This description will clearly enable one skilled in the
art to make and use the invention, and describes several embodiments,
adaptations, variations, alternatives and uses of the invention,
including what we presently believe is the best mode of carrying out
10 the invention.

A. Pre-monomer

Experimental Section

15 The following examples detail the two step synthesis process
of the mono-substituted premonomer. The synthesis of the
intermediate dibromoacetate is detailed in Example 1. Example 2 and
3 detail the synthesis of the 3-bromomethyl-3-methyloxetane
premonomer and the arylsulfonate of 3-hydroxymethyl-3-methyloxetane
premonomer respectively. $^1\text{H}/^{13}\text{C}$ NMR analysis was performed on a
20 Bruker MSL-300 spectrometer at 300 MHz in CDCl_3 solution with proton
and carbon shifts in ppm relative to tetramethylsilane. IR analysis
was performed on a Nicolet SX-5 spectrometer.

EXAMPLE A1

Preparation of

25 3-bromo-2-bromomethyl-2-methylpropyl Acetate

In a 12L flask equipped with an overhead stirrer, reflux condenser, and addition funnel was placed 1,1,1-tris(hydroxymethyl)ethane (TME, 1.000 Kg, 8.32 mol) and glacial acetic acid (3.750 L). The mixture was allowed to stir until partial dissolution of the TME had occurred and then the sodium bromide (2.568 Kg, 24.96 mol) was added with vigorous stirring. The sulfuric acid (1.718 Kg, 16.64 mol) was then slowly added over 6 hours. After the addition was complete, the reaction mixture was heated to 120°C for 48 hours. At this time GC evidence indicated that the reaction was complete and the mixture was cooled to room temperature and quenched with 7L of ice water. The organic and aqueous phases were separated and the organic was washed with water, 0.5N NaOH (until neutral pH), brine, and then dried over MgSO₄ to yield the product as a clear colorless oil in 92% yield (2.206 Kg): IR (KBr) 2980-2800, 1744, 1374, 1242, 1043, 710 cm⁻¹; ¹H NMR δ 1.20 (s, 3H), 2.11 (s, 3H), 3.48 (s, 4H), 4.09 (s, 2H); ¹³C NMR δ 20.12, 20.58, 38.21, 39.04, 67.08, 170.32.

EXAMPLE A2

Preparation of BrMMO Pre-monomer 3-Bromomethyl-3-methyloxetane

In a 50 L flask equipped with an overhead stirrer and reflux condenser was placed 3-bromo-2-bromomethyl-2-methylpropyl acetate (2.206 Kg, 7.66 mol), 3M NaOH (7.67 L, 22.98 mol), tetrabutylammonium bromide (123.47 g, 0.383 mol), and CCl₄ (7.66 L). The resulting

heterogeneous solution was then refluxed at 70°C overnight. At this time GC evidence indicated that the reaction was complete. The reaction was then cooled to room temperature. The organic and aqueous phases were separated, the organic phase was washed with water and brine, and then dried over MgSO₄. Removal of the solvent gave the product as a clear, light yellow oil (1.224 Kg) in 97% yield. Distillation gave a clear, colorless oil (1.189 Kg) in 94% yield, bp 46°C/0.3mm Hg; IR (KBr) 2980-2800, 1242, 1201, 1147, 704 cm⁻¹; ¹H NMR δ 1.44 (s, 3H), 3.65 (s, 2H), 4.40 (d, J = 5.8 Hz, 2H), 4.45 (d, J = 5.8 Hz, 2H) ¹³C NMR 22.38, 40.58, 41.29, 80.54.

Example A3

Preparation of Pre-monomer

p-Toluenesulfonate of 3-Hydroxymethyl-3-methyloxetane

A solution of 3-hydroxymethyl-3-methyloxetane (612g, 6 mol) in pyridine (800 ml) was cooled to -10 °C and treated, slowly, with a solution of p-toluenesulfonyl chloride (1364g, 7 mol) in pyridine (700 ml). The rate of addition was maintained so that the contents of the flask were kept below -5 °C. Upon complete addition, the solution temperature was held at -5 °C for 30 minutes and then at room temperature for 2 hours. The contents of the flask were quenched by pouring it into ice water (10 L), and the precipitated solid was filtered, washed with water and dried in air. The purity of the product as determined by GLC analysis was >98%. By this method, 1352 g of the desired product was obtained, representing an

88% yield.

The yield and purity of the bromomethyl and arylsulfonate premonomer product are extremely high and these examples clearly show how easily and inexpensively the mono-substituted premonomer of this invention is synthesized.

B. Monomer / Prepolymer Examples

Experimental

In the following examples, the polymerization was practiced with boron trifluoride etherate catalyst, although the currently preferred catalyst is boron trifluoride tetrahydrofuranate. Commercially available boron trifluoride etherate and boron trifluoride tetrahydrofuranate were distilled under reduced pressure prior to use. Similarly, the initiator, 1,4-butanediol, was purchased commercially and distilled from calcium hydride and stored over a 4 Å molecular sieve prior to use.

The polymerization was conducted in jacketed glass reactors equipped with a mechanical stirrer reflux condenser and a digital thermometer. ¹H, ¹³C and ¹⁹F NMR analysis were conducted on a Bruker MSL-300 spectrometer in deuterochloroform solution with proton and carbon chemical shifts reported in parts per million (ppm) relative to tetramethylsilane and fluorine shifts relative to trichlorofluoromethane. Infrared analysis was conducted on a Nicolet SX-5 spectrometer. Gel permeation chromatography (GPC) was conducted on a Waters gel permeation chromatograph equipped with four ultrastyrigel columns (100 Å, 500 Å, 10³ Å and 10⁴ Å) a differential

refractive index detector and a Data Module 730. THF was used as the mobile phase. The GPC was calibrated with a series of well characterized (i.e., M_n , M_w are well known) polystyrene standards (Narrow Standards), and thus the number average molecular weight (M_n) and weight average molecular weight (M_w) reported are expressed relative to styrene. Differential scanning calorimetry (DSC) was performed on a DuPont 990 thermal analyzer system at a heating rate of 10 °C/min. Elemental analysis was conducted by Galbraith Laboratories in Knoxville, Tennessee. Inherent viscosity of prepolymers was measured in THF at a concentration of 0.5 g/dL at 25 °C. Equivalent weights were determined by ^1H NMR employing trifluoroacetic anhydride (TFAA) end group analysis. Fluoroalcohols were purchased commercially from either 3M Corporation or DuPont Corporation, and, with the exception of DuPont's Zonyl BA-L alcohols, were used as received. Purification of the Zonyl BA-L alcohols is described in Example B6.

In Examples B1 and B2 we clearly establish proof of the reaction mechanism for the production of the fluorinated alkoxymethylene-3-methyloxetane monomer using the arylsulfonate pre-monomer.

EXAMPLE B1

Preparation of 3-FOX Monomer

3-(2,2,2-Trifluoroethoxymethyl)-3-methyloxetane.

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Synthesis of the 3-FOX oxetane monomer is performed as follows:

10 A dispersion of 50 weight percent (2.8 grams, 58.3 mmol) sodium hydride in mineral oil, was washed twice with hexanes and suspended in 35 milliliters of dimethyl formamide. Then, 5.2 grams (52 mmol) of trifluoroethanol was added and the mixture was stirred for 45 minutes. A solution of 10.0 grams (39 mmol) of 3-hydroxymethyl-3-methyloxetane p-toluenesulfonate in 15 milliliters of dimethyl formamide was added and the mixture was heated at 75-85°C for 20 hours, when ¹H MNR analysis of an aliquot sample showed that the starting sulfonate had been consumed.

20 The mixture was poured into 100 milliliters of ice water and extracted with 2 volumes of methylene chloride. The combined organic extracts were washed twice with water, twice with 2 weight percent aqueous hydrochloric acid, brine, dried over magnesium sulfate, and evaporated to give 6.5 grams of 3-(2,2,2-trifluoroethoxymethyl)-3-methyloxetane as an oil containing less than 1 weight percent dimethyl formamide. The yield of this product was 90 percent. The oil was distilled at 30°C and 0.2 millimeters mercury pressure to give 4.3 grams of analytically pure 3-FOX, corresponding to a 60 percent yield. The analyses of the product were as follows: IR (KBr) 2960-2880, 1360-1080, 990, 840 cm⁻¹; ¹H NMR δ 1.33 (s, 3H), 3.65

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(s, 2H), 3.86 (q, J=8.8 Hz, 2 H), 4.35 (d, J=5.6 Hz, 2 H), 4.51 (d, J=5.6 Hz, 2 H); ¹³C NMR δ 20.72, 39.74, 68.38 (q, J=40 Hz), 77.63, 79.41, 124 (q, J=272 Hz). The calculated elemental analysis for C₇H₁₁F₃O₂ is: C=45.65; H=6.02; F=30.95. The experimental analysis found: C=45.28; H=5.83; F=30.59.

EXAMPLE B2

Preparation of 7-FOX Monomer

3-(2,2,3,3,4,4,4-Heptafluorobutoxymethyl)- 3-methyloxetane

A 50 weight percent dispersion of sodium hydride (6.1 grams, 127 mmol) in mineral oil, was washed twice with hexanes and was suspended in 60 milliliters of dimethyl formamide. Then 24.0 grams (120 mmol) of 2,2,3,3,4,4,4-heptafluorobutan-1-ol was added and the mixture was stirred for 45 minutes. A solution of 25.0 grams (97.5 mmol) of 3-hydroxymethyl-3-methyloxetane p-toluenesulfonate in 15 milliliters of dimethyl formamide was added and the mixture was heated at 75-85°C for 30 hours when ¹H NMR analysis of an aliquot showed that the starting sulfonate had been consumed.

The mixture was poured into 100 milliliters of ice/water and extracted with two volumes of methylene chloride. The combined organic extracts were washed twice with water, twice with 2 weight percent aqueous hydrochloric acid, brine, dried over magnesium sulfate, and evaporated to give 27.5 grams of 3-(2,2,3,3,4,4,4-heptafluorobutoxymethyl)-3-methyloxetane (i.e., 7-FOX) as an oil. The oil was distilled at 33°C and 0.2 millimeters mercury pressure to give 12.2 grams of analytically pure ether, corresponding to a 44 percent yield. The experimental analyses were: IR (KBr) 2960-2880,

1280-1030, 995, 840 cm^{-1} , ^1H NMR 1.31 (s, 3 H), 3.67 (s 2 H), 3.99 (t, $J=13.3$ Hz, 2 H), 4.34 (d, $J=5.7$ Hz 2 H), 4.50 (d, $J=5.7$ Hz, 2 H); ^{13}C NMR δ 20.242, 39.627, 67.778, 77.730, 79.110, 108.72, 114.7, 117.58; ^{19}F NMR δ -81.4, -120.6, -128.1. The calculated elemental analysis for $\text{C}_8\text{H}_{11}\text{F}_8\text{O}_2$ is C=38.04; H=3.90; F=46.80. The experimental analyses found: C=38.03; H=3.65; and F=46.59.

Examples B3, B4 and B5 provide detail of the reaction mechanism for the synthesis of the 15-FOX, 13-FOX and a mixture of 13/17/21-FOX using the 3-chloromethyl-3-methyloxetane, the 3-bromomethyl-3-methyloxetane and the 3-iodomethyl-3-methyloxetanes as the premonomers, respectively. Note that although the perfluoroalkyl moiety on the side-chain increases in size, the substitution of the fluorinated alkoxide for the halogen proceeds and the yields are high. Further, we have clearly shown by way of Example B5 that a mixture of perfluorinated alkoxymethylene-3-methyloxetanes may be produced by merely introducing a mixture of fluorinated alcohols.

We also show that this reaction works for those fluorinated alcohols in which the fluoroalkyl is separated from the hydroxy group by 2 methylenes as well as by 1 methylene group (i.e., the process is equally effective for the DuPont alcohols as it is for the 3M alcohols).

EXAMPLE B3

PREPARATION OF 15-FOX

3-(2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-PENTADEC AFLUORO-OCTYLOXYMETHYL)-3-METHYLOXETANE

A dispersion of 50 weight percent sodium hydride (4.0 g, 83 mmol) in mineral oil was washed with hexanes and suspended in 200 milliliters of dimethylformamide. A solution of 30 grams of 2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-pentadecafluorooctan-1-ol (75 mmol) in 50 milliliters of dimethylformamide was added over a period of 3 hours, and the resulting mixture was stirred at room temperature for one hour. Next, a solution of 9.3 grams (77 mmol) of 3-chloromethyl-

3-methyloxetane in 20 milliliters of dimethylformamide was added and the resulting mixture was heated at 75°C. for 16 hours. The mixture was cooled to room temperature and slowly poured into 1 liter of ice/water and extracted with two volumes of Freon 113. The combined organic extracts were washed twice with water, once with 2 weight percent aqueous hydrochloric acid and once with brine, dried over magnesium sulfate, filtered, and evaporated to give 32 grams of crude product. The crude product was distilled under reduced pressure to give 26.5 grams (73%) of analytically pure 3-(2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-pentadecafluorooctoxymethyl)-3-methyloxetane (i.e., 15-FOX), an oil with a boiling point of 68 to 70°C./1.6 mm-Hg. The experimental analyses were: ¹H NMR (CDCl₃/Freon 113) δ 4.49 and 4.37 (AB, J=5.5 Hz, 4 H), 4.00 (triplet, J=13.2 Hz, 2 H), 3.70 (singlet, 2 H), and 1.32 (singlet, 3 H); ¹³C NMR δ 21.02, 40.33, 68.77 (triplet, J=146.2 Hz), 78.60, and 79.87 (signals from carbon bearing fluorine are not included due to complex splitting patterns and low peak intensities); ¹⁹F NMR δ -81.3 (3 F), -119.9 (2F), -122.6 (2 F), -123.3 (2 F), -123.5 (2 F), -123.9 (2 F) and -126.8 (2 F). The elemental analysis was: Calculated for C₁₃H₁₁F₁₅O₂: C, 32.2; H, 2.3; F, 58.9. Found: C, 32.2; H, 2.2; F, 58.3.

EXAMPLE B4

PREPARATION OF 13-FOX

3-(3,3,4,4,5,5,6,6,7,7,8,8,8-TRIDECAFLUORO-OCTYLOXYMETHYL)-3-METHYLOXETANE

In a manner similar to that described above, 12.0 grams of 3-bromomethyl-3-methyloxetane (73 mmol) was reacted with 26.5 grams of 3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctan-1-ol (72.7 mmol) in 300 milliliters of dimethylformamide in the presence of 3.9 grams of a 50 weight percent dispersion of sodium hydride (81 mmol) in mineral oil at 85°C. for 24 hours to give 21.5 grams (70% yield) of 3-(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyloxymethyl)-3-methyloxetane, a colorless oil with a boiling point of 66-68°C./2-2.5

mm-Hg; ¹H NMR (CDCl₃) δ 4.50 and 4.36 (AB, J=5.5 Hz, 4 H), 3.78 (t, J=6.6 Hz, 2 H), 3.53 (s, 2 H), 2.42 (triplet of triplets, J=6.6 and 18 Hz, 2 H), and 1.31 (s, 3 H); ¹³C NMR (CDCl₃) δ 79.89, 78.30, 63.31, 39.9, 31.64 (t), and 21.1 (signals due to carbons bearing fluorines are not included due to the complex splitting patterns and low peak intensities); ¹⁹F NMR δ -81.4 (3 F), -113.8 (2 F), -118.2 (2 F), -112.3 (2 F), -124.1 (2 F) and -126.7 (2 F). The elemental analysis was: Calculated for C₁₃H₁₃F₁₃O₂: C, 34.8; H, 2.9; F, 55.1. Found: C, 35.1; H, 3.0; F, 54.7.

Note that the fluorinated alcohols in Examples B4 and B6 were supplied by DuPont (i.e., R_f-CH₂CH₂OH). These alcohols are inexpensive and available in bulk, however, they are not pure and must be purified prior to use in these reactions. Example B5 details how these fluoroalcohols may be purified. On the other hand, the fluoroalcohols of Examples B1, B2 and B3 have a methanol group pendant to the perfluoroalkyl moiety (i.e., R_f-CH₂OH) and are purchased From 3M Corporation as reagent grade, not requiring further purification.

EXAMPLE B5 PURIFICATION OF COMMERCIAL FLUOROALCOHOLS

Zonyl BA-L is a narrow distribution, oligomeric mixture of fluoroalcohols that is available from Dupont Chemicals in pilot plant quantities. Zonyl BA-L is a yellow liquid which by GLC is a mixture of the following oligomers: 3-(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctan-1-ol (C₈, 60%); 3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecan-1-ol (C₁₀, 26%); 3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,12,12,12-heneicosafuorododecanol (C₁₂, 6%); and various unidentified high boiling compounds (8%). Zonyl BA-L was washed with equal volumes of 10 weight percent aqueous sodium thiosulfate, 10 weight percent aqueous sodium bicarbonate (to remove HF), water and brine, dried,

filtered, and distilled under reduced pressure (3 mm-Hg) at 50-100°C. to give a mixture of 69% C8, 26% C10 and 5% C12 in 83% yield.

EXAMPLE B6

PREPARATION OF A MIXTURE: 13/17/21-FOX

3,3,4,4,5,5,6,6,7,7,8,8,8-TRIDecafluorooctyloxymethyl-,
3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-
HEPTaDecafluorodecyloxymethyl-,
AND

3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,12,12,12-
HENEICosafluorododecyloxymethyl-3-METHYLOXETANE

In a manner similar to that described above, a mixture of 69% C8, 26% C10 and 5% C12 fluoroalcohols (distilled Zonyl BA-L from Example B5, 51.6 grams, 129 mmol) was reacted with 27 grams of 3-iodomethyl-3-methyloxetane (127 mmol) in 500 milliliters of dimethylformamide at 85°C. for 18 hours to give 60 grams of crude product. The crude product was fractionally distilled through a 6" Vigerux column to yield the following fractions: Fraction #1 (4.8 grams) was collected between 25°C. and 45°C. at 3.5-2.9 mm-Hg, and was a mixture of unreacted fluoroalcohols. Fraction #2 (2.8 grams) was collected at 45-71°C./0.7-3.0 mm-Hg, and was a mixture of unreacted fluoroalcohols and fluorinated oxetane monomers. The final fraction (49 grams, 80%), boiling at 70-85°C./0.7-0.9 mm-Hg, was a mixture of 73% 3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyloxymethyl-3-methyloxetane (13-FOX), 24% 3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecyloxymethyl-3-methyloxetane (17-FOX), and 3% 3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,12,12,12-heneicosafuorododecyloxymethyl-3-methyloxetane (21-FOX), a colorless oil with a boiling point of 70-85°C./0.7-0.9 mm-Hg; ¹H NMR (CDCl₃) δ 4.50 and 4.35 (AB, J=5.9 Hz, 4 H), 3.78 (t, J=6.6 Hz, 2 H), 3.53 (s, 2 H), 2.42 (tt, J=6.6 and 17.6 Hz, 2 H), and 1.31 (s, 3 H); ¹³C NMR δ 21.3, 31.86 (t, J=130.1 Hz), 40.2, 63.6, 76.8, and 80.2 (signals for carbons bearing fluorine are not included due to complex splitting patterns and overlap of signals; ¹⁹F NMR δ -81.5, -113.8,

-122.3, -123.3, -124.1, -124.5, -125.8, and 126.7.

Phase Transfer Catalyst Process

5 Examples B7 and B8 provide details as to the preferred process for synthesizing the FOX monomers of this invention using a phase transfer catalyst (PTC).

EXAMPLE B7

10 Preparation of 7-FOX Using PTC Process

3-(2, 2, 3, 3, 4, 4, 4-HEPTAFLUOROBUTOXYMETHYL)-3-METHYLOXETANE

15 A 2 L, 3 necked round bottom flask fitted with a reflux condenser, a mechanical stirrer, a digital thermometer and an addition funnel was charged with 3-bromomethyl-3-methyloxetane (351.5 g, 2.13 mol), heptafluorobutan-1-ol (426.7 g, 2.13 mol), tetrabutylammonium bromide (34.4 g) and water (85 ml). The mixture was stirred and heated to 75 °C. Next, a solution of potassium hydroxide (158 g, 87% pure, 2.45 mol) in water (200 ml) was added and
20 the mixture was stirred vigorously at 80-85 °C for 4 hours. The progress of the reaction was monitored by GLC and when GLC analysis revealed that the starting materials were consumed, the heat was removed and the mixture was cooled to room temperature. The reaction mixture was diluted with water and the organic layer was separated
25 and washed with water, dried and filtered to give 566 g (94%) of crude product. The crude product was transferred to a distillation flask fitted with a 6 inch column and distilled as follows:

- 30 - Fraction #1, boiling between 20°C-23°C/10 mm-Hg, was found to be a mixture of heptafluorobutanol and other low boiling impurities, was discarded;
- Fraction #2, boiling between 23°C and 75°C/1 mm-Hg, was found to be a mixture of heptafluorobutanol and 7-FOX, was also discarded; and
- 35 - Fraction #3, boiling at 75°C/1 mm-Hg was >99% pure 7-FOX representing an overall yield of 80.2%

NMR and GLC data revealed that 7-FOX produced by this method was identical to 7-FOX prepared using the sodium hydride/DMF process.

EXAMPLE B8

Preparation of 15-FOX Using PTC Process

3-(2, 2, 3, 3, 4, 4, 5, 5, 6, 6, 7, 7, 8, 8, 8-PENTADEC AFLUORO OCTYLOXY METHYL)-3-METHYLOXETANE

In a manner similar to the that of Example B14, a mixture of 3-bromomethyl-3-methyloxetane (468 g, 2.84 mol), 2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-pentadecafluorooctan-1-ol (1032g, 2.58 mol), tetrabutylammonium bromide (41.5 g), potassium hydroxide (208 g, 3.23 mol), and water (1680 ml) was heated under reflux for 3 hours. GLC analysis revealed complete consumption of starting materials. The reaction mixture was diluted with water, worked-up in the usual manner, and distilled under reduced pressure to give 1,085 g of 15-FOX, representing an overall yield of 87%; bp 82°C/0.1 mm-Hg. The distilled material was >99% pure as indicated by GLC and was used in subsequent polymerization reactions.

The first of three Comparative Examples below show that we are able to easily synthesize, using the process of our invention, in high yield, the bis-equivalent to our 3-FOX monomer.

In the second Comparative Example we show that we can easily homopolymerize, using the process of our invention, the bis 3-FOX to produce the bis 3-FOX prepolymer. As expected and consistent with the technology of Falk et al., the bis-prepolymer of this Comparative Example was a white waxy crystalline solid, unlike the low viscosity oils of the prepolymers of this invention. This is attributable to the ordered structure of the fluoroalkoxy side-chains resulting in efficient packing of the prepolymers into a crystalline structure.

In the third Comparative Example we show that a bis-monomer

having much longer fluoroalkoxy side-chains may still be homopolymerized by the process of this invention. In other words, the homopolymerization of the bis-monomer is not limited by the size of the fluoroalkoxy groups. This is unexpected in view of the difficulties described in the background in achieving homopolymerization of the bis-substituted oxetanes. However, we observe that as the fluorinated side-chains of the bis-monomer become larger, homopolymerization results in a much higher fraction of the undesirable, non-functional cyclic tetramer. In our third Comparative Example the initial fraction of the cyclic tetramer byproduct is 32%. Even after further purification, the cyclic tetramer was still present at 9%. It is hypothesized that the presence of the cyclic tetramer impurity resulted in the prepolymer being a liquid rather than the expected solid, as it is well known that impurities will prevent crystallization. Increasing the size of the fluorinated side-chains results in increasing yields of the cyclic tetramer impurity and lower yields of the prepolymer. This suggests that the homopolymerization of the bis-monomer, although possible by the process of this invention, may not be commercially desirable for those bis-monomers having larger side-chains. In comparison, the FOX prepolymers of this invention do not exhibit decreasing yields/quality with increasing side-chain length. Consequently, the FOX prepolymers of this invention make possible the economic production of fluorinated polyurethanes having outstanding surface properties (see Exhibit 1).

COMPARATIVE EXAMPLE B9-a

Preparation of Bis-3-FOX

3,3-Bis-(2,2,2-trifluoroethoxymethyl)oxetane

A 50 weight percent dispersion of sodium hydride in 18.4 grams (0.383 mol) of mineral oil, was washed twice with hexanes and was suspended in 200 milliliters of dimethyl formamide. Then, 38.3 grams (0.383 mol) trifluoroethanol was added dropwise over 45 minutes while hydrogen gas evolved. The mixture was stirred for 30 minutes

and a solution of 30.0 grams (0.073 mol) of 3,3-bis(hydroxymethyl)oxetane di-p-toluenesulfonate in 50 milliliters of dimethyl formamide was added. The mixture was heated to 75°C for 64 hours when ¹H NMR analysis of an aliquot showed that the starting sulfonate had been consumed.

The mixture was poured into water and extracted with two volumes of methylene chloride. The combined organic extracts were washed with brine, 2 weight percent aqueous hydrochloric acid, water, dried over magnesium sulfate, and evaporated to give 17.5 grams of 3,3-bis(2,2,2-trifluoroethoxymethyl)oxetane as an oil containing less than 1 weight percent dimethyl formamide. The oil was purified by bulb-to-bulb distillation at 42-48°C and 10.1 millimeters mercury pressure to give 15.6 grams of analytically pure bis-3-FOX, corresponding to a 79 percent yield. The analyses of the product were as follows: ¹H NMR δ 3.87 (q, J=8.8 Hz, 4 H), 4.46 (s, 4 H); ¹³C NMR δ 43.69, 68.62 (q, J=35 Hz), 73.15, 75.59, 123.87 (q, J=275 Hz); ¹⁹F NMR δ -74.6 (s). The calculated elemental analysis for C₉H₁₂F₆O₃ is: C=38.31; H=4.29; and F=40.40. The experimental analyses found: C=38.30; H=4.30; and F=40.19.

COMPARATIVE EXAMPLE B9-b

Preparation of the Bis-3-FOX Prepolymer Poly 3,3-bis(2,2,2-trifluoroethoxymethyl)oxetane

A solution of 33.9 milligrams (0.378 mmol) of butane-1,4 diol and 106.3 milligrams (0.75 mmol) of boron trifluoride etherate in 3.8 grams of methylene chloride was stirred at ambient temperature for 15 minutes under nitrogen in a dry polymerization flask. The solution was cooled to 1.5°C and a solution of 1.88 grams (6.67 mmol) of 3,3-bis(2,2,2-trifluoroethoxymethyl)oxetane in 2.3 grams of methylene chloride was added. The resultant solution was stirred for 16 hours at 1-2°C at which time ¹H NMR analysis of an aliquot indicated that the starting oxetane had been consumed.

The solution was warmed to ambient temperature and quenched with water. The organic layer was washed with brine, 2 percent aqueous hydrochloric acid, and evaporated to give 1.62 grams of poly 3,3-bis(2,2,2-trifluoroethoxymethyl)oxetane, corresponding to 85% yield. The prepolymer was a white, waxy solid. The polymer analyses were: DSC mp 80.96°C (26.35 Joules/gram); GPC: M_n =5321, M_w =7804, polydispersity = 1.47; inherent viscosity 0.080 dL/g; ^1H NMR δ 1.60 (broad singlet), 3.36 (s, 4 H), 3.58 (s, 4 H), 3.79 (q, 4 H); ^{13}C NMR 45.49, 68.25 (q, J=33 Hz), 69.20, 70.97, 123.81 (q, J=280 Hz).

COMPARATIVE EXAMPLE B9-c

Homopolymerization of Bis-Monomer

3,3-BIS(2,2,3,3,4,4,4-HEPTAFLUOROBUTOXYMETHYL) OXETANE

In a manner similar to that described in Example B7-b, a solution of 252 grams of 3,3-bis(2,2,3,3,4,4,4-heptafluorobutoxymethyl) oxetane (523 mmol) in 75 milliliters of Freon 113 was added to a mixture of 1.05 grams of boron trifluoride tetrahydrofuranate (7.5 mmol) and 0.265 gram of 1,4-butanediol (2.93 mmol) in 178 milliliters of methylene chloride at 10°C. The mixture was stirred at room temperature for 48 hours at which time NMR analysis of an aliquot indicated 96 percent conversion. The reaction was quenched with water and the polymer was precipitated into methanol to give, after drying at 80°C./2 mm-Hg for 16 hours, 211 grams of poly 3,3-bis (2,2,3,3,4,4,4-heptafluorobutoxymethyl) oxetane, a colorless oil in 84 percent yield. GPC analysis of this oil revealed it was a mixture of 68% linear and 32% cyclic materials. The cyclic product was isolated and identified as the cyclic tetramer, a white waxy solid with a melting point of 80°C; ^1H NMR δ 3.87 (t, J=13.5 Hz, 4 H), 3.54 (s, 4H), and 3.32 (S, 4H) (No end groups were observed on addition of trifluoroacetic anhydride); ^{13}C NMR δ 71.2, 68.6, 68.4 (t), and 46.2 (signals due to carbons bearing fluorine are not included).

The above oil was further purified by first dissolving the

material in methylene chloride/Freon 113 (75:25 mixture), precipitating the polymer into a 10 fold excess of methanol, stirring the precipitated oil with tetrahydrofuran at room temperature for 2 days, and finally separating and drying the insoluble fraction at 85°C. at 2 mm-Hg for 16 hours. This yielded 128 grams of a clear, viscous oil, corresponding to 51% overall yield. The oil by GPC analysis was determined to be a mixture of 91% linear polymer and 9% cyclic tetramer. The polymer analyses were: GPC: $M_n=5,526$, $M_w=7,336$, polydispersivity = 1.32; ^1H NMR ($\text{CDCl}_3/\text{Freon 113}/\text{TFAA}$) δ 3.39 (s, 4 H), 3.59 (s, 4 H), 3.87 (t, $J=13.5$ Hz, 4 H) and 4.40 (s, $-\text{CH}_2\text{OCOCF}_3$); Equivalent Weight based on ^1H NMR = 2,600; ^{13}C NMR ($\text{CDCl}_3/\text{Freon 113}$) δ 46.4, 68.5 (t), 70.1 and 72.1 (signals from carbons bearing fluorines are not included).

Examples B10 through B15 provide details on the polymerization of the FOX monomers to provide the FOX prepolymers of this invention.

Examples B10, B11 and B12 detail the homopolymerization of the 3-FOX, 7-FOX and 13-FOX respectively to provide random, asymmetrical prepolymers. Note that the yield of the 7-FOX prepolymer of Example B11 produced from the 7-FOX mono-substituted monomer resulted in a much higher yield of the prepolymer than that obtained from the bis-7-FOX homopolymerization of Comparative Example B9-c (83% versus 51%).

Example B12 uses the preferred $\text{BF}_3 \cdot \text{THF}$ catalyst.

EXAMPLE B10

Homopolymerization of 3-FOX 3-(2,2,2-Trifluoroethoxymethyl)- 3-methyloxetane

A solution of 34.3 milligrams (0.38 mmol) of butane-1,4-diol and 109.7 milligrams (0.77 mmol) of boron trifluoride etherate in 4 grams of methylene chloride was stirred at ambient temperature for 15

minutes under nitrogen in a dry polymerization flask. The solution was cooled to 1.5°C and a solution of 1.20 grams (6.52 mmol) of 3-(2,2,2-trifluoroethoxymethyl)-3-methyloxetane in 1.3 grams of methylene chloride was added. The resultant solution was stirred for 5 hours at 1-2°C at which time ¹H NMR analysis of an aliquot indicated that the starting oxetane had been consumed. The solution was warmed to ambient temperature and quenched with water. The organic layer was washed with brine, 2 weight percent aqueous hydrochloric acid, and evaporated to give 1.053 grams of poly-3-(2,2,2-trifluoroethoxymethyl)-3-methyloxetane as an oil, corresponding to a 88 percent yield. The polymer analyses were: DSC T_g -45°C, decomposition temperature was greater than 200°C; GPC M_n=7376, M_w=7951, polydispersity 1.08, inherent viscosity 0.080 dL/g; Equivalent Weight by ¹H NMR = 6300; ¹H NMR δ 0.95 (s, 3 H), 3.26 (m, 4 H), 3.52 (s, 2 H) 3.84 (q, 2 H); ¹³C NMR δ 17.57, 42.09, 69.30 (q, J=33 Hz), 74.42, 75.90, 125.18 (q, J=280 Hz).

EXAMPLE B11

Homopolymerization of 7-FOX

Poly-3-(2,2,3,3,4,4,4-heptafluorobutoxymethyl)-3-methyloxetane

A solution of 34.7 milligrams (0.38 mmol) of butane-1,4-diol and 109.7 milligrams (0.77 mmol) of boron trifluoride etherate in 3.4 grams of methylene chloride was stirred at ambient temperature for 15 minutes under nitrogen in a dry polymerization flask. The solution was cooled to 1.5°C and a solution of 2.00 grams (7.08 mmol) of 3-(2,2,3,3,4,4,4-heptafluorobutoxymethyl)-3-methyloxetane (i.e., 7-FOX) in 3.3 grams of methylene chloride was added. The resultant solution was stirred for 4 hours at 1.2°C; at which time ¹H NMR analysis of an aliquot indicated that the starting oxetane had been consumed.

The solution was warmed to ambient temperature and quenched with water. The organic layer was washed with brine, 2 percent aqueous hydrochloric acid, and evaporated to give 1.65 grams of poly-

3-(2,2,3,3,4,4,4-heptafluorobutoxymethyl)-3-methyloxetane, corresponding to a 83% yield. The prepolymer was an oil and had the following analyses: GPC $M_n=4066$, $M_w=5439$, polydispersity=1.34, inherent viscosity 0.054 dL/g.

5 This oil was further extracted with methanol and dried to give 1.46 grams of poly-7-FOX, corresponding to 72% yield, and has the following analyses: DSC: $T_g = -45^\circ\text{C}$; GPC: $M_n=4417$, $M_w=5658$, polydispersity = 1.28; inherent viscosity = 0.056 dL/g; Equivalent weight by ^1H NMR = 6359, ^1H NMR δ 0.93 (s, 3 H), 3.24 (m, 4 H), 3.48 (s, 2 H), 3.92 (q, $J=13.6$ Hz, 2 H); ^{13}C MMR 16.14, 40.57, 67.37 (t), 10 72.89, 74.76 (signals from carbon-bearing fluorine are not included).

EXAMPLE B12

Homopolymerization of 13-FOX

3-(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyloxymethyl)-3-METHYLOXETANE

20 In a manner similar to that described in Example B9, a solution of 10 grams of 3-(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyloxymethyl)-3-methyloxetane (22.3 mmol) in three milliliters of Freon 113 was added dropwise to a mixture of 109 milligrams of boron trifluoride tetrahydrofuranate (0.78 mmol) and 35 milligrams of 1,4-butanediol (0.39 mmol) in methylene chloride at 25 10°C . The mixture was stirred at room temperature for 24 hours, quenched with water, and precipitated in methanol to give, after drying at $80^\circ\text{C}/2$ mm-Hg for 16 hours, 8.3 gram of poly 3-(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyloxymethyl)-3-methyloxetane, a clear colorless oil. The polymer analyses were: 30 Inherent viscosity = 0.067 dL/g; GPC: $M_n = 5,340$, $M_w = 6,620$, Poly Dispersity = 1.24; DSC, $T_g = -38^\circ\text{C}$; ^1H NMR ($\text{CDCl}_3/\text{Freon 113/trifluoroacetic anhydride (TFAA)}$) δ 3.67 (t, 5.9 Hz, 2 H), 3.31 (s, 2 H), 3.21 (m, 4 H), 2.35 (m, 2 H), and 0.93 (s, 3 H); ^1H NMR ($\text{CDCl}_3/\text{Freon 113}$) 0.95 (s, 3 H), 2.37 (br t, $J=18.3$ Hz, 2 H), 3.25 (m,

4 H), 3.35 (s, 2H), 3.71 (t, 6.0 Hz, 2 H), and 4.30 (s, $-\text{CH}_2\text{OCOCF}_3$); Equivalent Weight based on ^1H NMR was 4,756, ^{13}C NMR ($\text{CDCl}_3/\text{Freon 113}$) δ 17.35, 31.75, 41.5, 63.4, 74.1 and 74.3 (signals from carbon bearing fluorine are not included).

Examples B13 - B15 provide details as to the copolymerization of various FOX monomers to provide FOX co-prepolymers. The polymerization in all three Examples is catalyzed with $\text{BF}_3\text{-THF}$. Noteworthy is the high yields in the 80%-85% in all three Examples.

EXAMPLE B13

Copolymerization of 3-FOX and 7-FOX

3-(2,2,2,-TRIFLUOROETHOXYMETHYL)-3-METHYLOXETANE

WITH

3-(2,2,3,3,4,4,4-HEPTAFLUOROBUTOXYMETHYL)-3-METHYLOXETANE

In a manner similar to that described in Example B9, a solution of 35 grams of 3-(2,2,2,-trifluoroethoxymethyl)-3-methyloxetane (190 mmol) and 183 grams of 3-(2,2,3,3,4,4,4-heptafluorobutoxymethyl)-3-methyloxetane (644 mmol) in 50 milliliters of 1,1,2-trichlorotrifluoroethane was added to a mixture of 0.390 gram of 1,4-butanediol (4.33 mmol), 1.55 grams of boron trifluoride tetrahydrofuranate (11.1 mmol), and 100 milliliters of methylene chloride at 18°C . The mixture was stirred at 18°C for 3 hours, quenched with water, and precipitated into methanol to give, after drying at $85^\circ\text{C}/2\text{ mm-Hg}$ for 16 hours, 186 grams of a clear, colorless oil, corresponding to 85% yield. NMR analysis revealed that this material was a 22:78 random copolymer of the above two monomers.

The polymer analyses were: DSC, $T_g = -42^\circ\text{C}$.; GPC: $M_n = 15,660$, $M_w = 30,640$; Polydispersity = 1.96; Equivalent Weight by ^1H NMR was 9,200; Inherent viscosity = 0.071; ^1H NMR ($\text{CDCl}_3/\text{Freon 113}$) δ 0.91 (s, CH_3), 3.22 (m, backbone $-\text{CH}_2-$), 3.44 (s, $-\text{CH}_2\text{O}$), 3.79 (q, $J = 8.8\text{ Hz}$, $-\text{CH}_2\text{CF}_3$) and 3.86 (t, $J = 13.5\text{ Hz}$, $-\text{CH}_2\text{C}_3\text{F}_7$); ^1H NMR $\text{CDCl}_3/\text{Freon}$

113/Trifluoroacetic anhydride) δ 0.95 (s, $-\text{CH}_3$), 3.23 (m, backbone $-\text{CH}_2-\text{S}$), 3.46 (s, $-\text{CH}_2\text{O}$), 3.77 (q, $J=8.6$ Hz, $-\text{CH}_2\text{CF}_3$), 3.87 (t, $J=13.5$ Hz, $-\text{CH}_2\text{C}_3\text{F}_7$), and 4.31 (s, $-\text{CH}_2\text{OCOCF}_3$); ^{13}C NMR ($\text{CDCl}_3/\text{Freon 113}$) δ 17.3, 41.6, 41.8, 68.6 (t), 69.3 (q), 74.2, 75.6, and 75.9 (signals from carbons bearing fluorine are not included).

In a similar manner, random copolymers of above monomers in 50:50 and 75:25 ratios were also prepared. The copolymers were clear, colorless oils that were soluble in tetrahydrofuran, methylene chloride and 1,1,2-trichlorotrifluoroethane (Freon 113).

EXAMPLE B14

Copolymerization of 3-FOX and 15-FOX

3-(2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-PENTADEC AFLUORO OXYMETHYL)-
3-METHYLOXETANE WITH
3-(2,2,2-TRIFLUOROETHOXYMETHYL)-3-METHYLOXETANE

A one-liter, three-necked, round-bottomed flask was fitted with a mechanical stirrer, nitrogen inlet/outlet tubes, a reflux condenser, a thermometer, and a constant addition funnel. The apparatus was dried with a heat gun, cooled under nitrogen to room temperature, and charged with a mixture of 0.914 grams of trimethylolpropane (TMP, 6.52 mmol), 3.1 grams of boron trifluoride tetrahydrofuranate (22 mmol), 160 milliliters of 1,1,2-trichlorotrifluoroethane and 30 milliliters of anhydrous methylene chloride. The mixture was stirred at room temperature for 30 minutes, cooled to 10°C ., and then treated, dropwise, with a solution of 106 grams of 3-(2,2,2-trifluoroethoxymethyl)-3-methyloxetane (576 mmol) and 94 grams of 3-(2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-pentadecafluorooctyloxymethyl)-3-methyloxetane (195.2 mmol) in 40 milliliters of 1,1,2-trichlorotrifluoroethane. A mild exotherm was observed in addition of the monomer. The reaction temperature was maintained at 18°C . for 2 hours and then at 25°C . for 4 hours at which time NMR analysis of an aliquot indicated that 98 percent of the oxetane monomers were consumed. The reaction mixture was diluted with 50 milliliters of methylene chloride and 50 milliliters of

1,1,2,-trichlorotrifluoroethane, and quenched with 50 milliliters of water. The organic layer was separated, washed with two equal volumes of water, and added dropwise to a 10 fold excess of methanol at room temperature. The precipitated oil was separated and redissolved in a 50:50 mixture of methylene chloride and 1,1,2-trichlorotrifluoroethane and transferred to a 500-milliliter, round-bottomed flask. The solvent was evaporated under reduced pressure and the resulting oil was dried at 85°C./2 mm-Hg for 16 hours to give 170 grams of a clear, colorless, viscous oil, corresponding to 85 percent yield. The NMR analyses of this material indicated it was a random copolymer of the above two monomers in a 74:26 ratio. The polymer analyses were: DSC, $T_g = -40^\circ\text{C}.$; GPC: $M_n = 6,178$, $M_w = 7,286$; Polydispersity = 1.18; Equivalent Weight by ^1H NMR was 3,520; Inherent viscosity was 0.065; ^1H NMR (CDCl_3) δ 0.94 (s, $-\text{CH}_3$), 3.23 (m, backbone $-\text{CH}_2\text{'S}$), 3.47 (s, $-\text{CH}_2\text{O}$), 3.75 (q, $J=8.6$ Hz, $-\text{CH}_2\text{CF}_3$) and 3.85 (t, $J=13.5$ Hz, $-\text{CH}_2\text{C}_3\text{F}_7$); ^1H NMR ($\text{CDCl}_3/\text{Trifluoroacetic anhydride}$) δ 1.00 (s, $-\text{CH}_3$), 3.37 (m, backbone $-\text{CH}_2\text{'S}$), 3.49 (s, $-\text{CH}_2\text{O}$), 3.78 (q, $J=8.6$ Hz, $-\text{CH}_2\text{CF}_3$), 3.96 (t, $J=13.5$ Hz, $-\text{CH}_2\text{C}_3\text{F}_7$), and 4.30 (s, $\text{CH}_2\text{OCOCF}_3$); ^{13}C NMR (CDCl_3) δ 17.1, 41.2, 41.3, 68.5 (t), 68.9 (q), 73.7, 75.3 and 75.5.

In a manner similar to that described above, random copolymers of above monomers in 50:50, 33:67, 25:75 and 10:90 ratios were also prepared. These copolymers were clear, colorless oils that were soluble in a solvent mixture of methylene chloride and 1,1,2,-trichlorotrifluoroethane.

EXAMPLE B15

Copolymerization of a mixture of 13-FOX, 17-FOX and 21-FOX

3,3,4,4,5,5,6,6,7,7,8,8,8-

TRIDECAFLUOROOCTYLOXYMETHYL-,

3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-

HEPTADEC AFLUORODECYLOXYMETHYL-, AND

3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,12,12,12-

HENEICOSAFLUORODODECYLOXYMETHYL-3-METHYLOXETANES

In a manner similar to that described in Example B12, a solution of 30 grams of 13-FOX (73%), 17-FOX (24%), and 21-FOX (3%) monomers (62 mmol) in 10 milliliters of Freon 113 was added dropwise to a mixture of 300 milligrams of boron trifluoride tetrahydrofuranate (2.14 mmol) and 95 milligrams of 1,4-butanediol (1.05 mmol) in 30 milliliters of methylene chloride at 10°C. The mixture was stirred at room temperature for 24 hours, quenched with water, and precipitated in methanol to give, after drying at 80°C./2 mm-Hg for 16 hours, 24 grams of the title copolymer, corresponding to 80 percent yield. The copolymer was a colorless, viscous oil. The analysis of the co-prepolymer was: Inherent viscosity = 0.075 dL/g; GPC: M_n = 6,639, M_w = 9,368, Polydispersity = 1.41; ^1H NMR (CDCl_3 /Freon 113/TFAA) δ 0.95 (s, 3 H), 2.37 (br t, $J=18.3$ Hz, 2 H), 3.25 (m, 4 H), 3.35 (s, 2H), 3.71 (t, 6.0 Hz, 2 H), and 4.30 (AB, $-\text{CH}_2\text{OCOCF}_3$); Equivalent Weight based on ^1H NMR was 2,510; ^{13}C NMR (CDCl_3 /Freon 113) δ 17.35, 31.75 (5), 41.1, 41.5, 63.4, 74.1 and 74.3.

C. ELASTOMERS

The FOX prepolymers of this invention can be cured with diisocyanates or polyisocyanates for the production of polyurethane elastomers. Detailed descriptions of the preferred method of making these elastomers are provided below.

EXPERIMENTAL

Mechanical properties (Stress-Strain analysis) were measured

with a Model 1122 Instron tester. Static contact angles of water with the polymer surface were measured with a Goniometer using doubly distilled water. Differential scanning calorimetry (DSC) and Thermogravimetric Analysis (TGA) were performed on a DuPont 990 thermal analyzer system. DSC measurements were made at a heating rate of 10°C/min in air, whereas TGA measurements were made at a heating rate of 20°C/min in air at a flow rate of 20 mL/min. Peel strength was measured with an Instron. Chemical resistance was measured by immersing the samples in selected solvents, removing the samples from the solvent after 24 h, and measuring the change in weight and dimensions. Surface energy was measured by the method of Wu et al. Isocyanates such as isophorone diisocyanate (IPDI), saturated methylenediphenyl diisocyanate (Des-W), N-100 and N3200 were obtained from Mobay Chemical Co. Isophorone diisocyanate (IPDI), was distilled prior to polymerization. 4,4'-Methylene dianiline (MDA) and solvents were purchased from Aldrich Chemical Co., whereas Jeffamine was obtained from Texaco Corporation. Isonal 93 was obtained from Dow Chemical Corporation.

EXAMPLE C1

Preparation of Poly 7-FOX/Des-W/Isonol Polyurethane Elastomer

This example illustrates the preparation of a polyurethane elastomer from the Homo-prepolymer of 3-(2,2,3,3,4,4,4-heptafluorobutoxymethyl)-3-methyloxetane (Poly 7-FOX) with the Des-W diisocyanate and the Isonol 93 cross-linker.

Note that the surface energy of the resulting 7-FOX polyurethane is 13.2 ergs/cm² which is a significant improvement over the surface energy of Teflon at 18.5 ergs/cm².

Procedure A (No solvent; casting a bulk article)

A 50 mL, 3-necked flask was dried with a heat gun under nitrogen and charged with Poly 7-FOX (10.005 g, 2.22 meq), Isonol 93 (107 mg, 1.21 meq), Des-W (469 mg, 98.5% pure, 3.50 meq), and

dibutyltin dilaurate (3 mg). The contents were mixed and casted into a Teflon mold. The mixture was then degassed, placed in an oven, and cured at 65°C for 16 h. The polymer sample was removed from the mold and characterized as follows:

5	Nature:	Tack-free Elastomer
	Color:	Opaque
	Static Contact Angle (H ₂ O)	117°
	Surface Energy	13.2 ergs/cm ²
	Mechanical Properties	
10	- Tensile Modulus	41 psi
	- Elongation at Break	1308%
	- Tensile Strength	622 psi
	Hardness	7 Shore A
	Glass Transition Temperature, DSC	-45°C
15	Thermal Stability, TGA	0% Wt. Loss to 260°C
	- Onset of major degradation	275°C
	Peel Strength, EPDM Rubber	9.5 lb/in, Adhesive Failure
	Water Absorption	
	- 9 days/25°C	0.16% by Weight Gain
20	- 16 h/100°C	0.28% by Weight Gain
	Chemical Resistance	
	- Stable	Methanol, hexane, toluene, 20% sodium hydroxide, non- leaded gasoline, & DMF
25	- Swell	THF, MTBE and Freon 113

EXAMPLE C2

30 Preparation of Poly 3/7-FOX/IPDI/MDA Polyurethane Elastomer

This example illustrates the preparation of polyurethane elastomer from a 25:75 Co-prepolymer of 3-(2,2,2-trifluoroethoxymethyl)-3-methyloxetane and 3-(2,2,3,3,4,4,4-

heptafluorobutoxymethyl)-3-methyloxetane (Poly 3/7-FOX, 25:75).

Note that this Example describes polymerization in a solvent, therefore the solution can be used to prepare thin polyurethane elastomer coatings. Application of the coating may be by any conventional means including dip-coating, spray coating, etc.

Procedure B (Polymerization in solvent for a bulk or coated article):

A 50 mL, 3-necked round bottom flask fitted with a condenser, a mechanical stirrer, thermometer, and a nitrogen inlet/outlet was dried under nitrogen and charged with the title co-prepolymer (2.93 g, 0.651 meq), IPDI (0.298 g, 2.68 meq), dibutyltin dilaurate (16 mg), and anhydrous tetrahydrofuran (6 mL). The mixture was heated under reflux for 2.5 h, cooled to room temperature and treated with a solution of methylene dianiline (0.120 g, 98.5% pure, 2.38 meq) in tetrahydrofuran (1.5 mL). The resulting yellow solution was stirred at room temperature for 16 h, casted into a teflon mold*, and the solvent was slowly evaporated at room temperature to give a yellow tacky material. This material was cured at 65°C for 24 h to give a tough, tack-free, elastomer. This material exhibited a contact angle with water of 112°. The mechanical properties of this elastomer were: tensile modulus, 48 psi; elongation at break, 941%; and tensile strength, 214 psi. The polymer sample was insoluble in methanol, toluene, ethanol and hexane, but swelled in Freon 113 and THF.

* Alternately, the substrate can be dip-coated or sprayed and cured in an oven at 65°C for 24 h to give a thin, continuous film, tack-free coating.

EXAMPLE C3

Preparation of Poly 3/7-FOX/IPDI/TMP Polyurethane Elastomer

This example illustrates the preparation of polyurethane

elastomer from a 25:75 Co-prepolymer of 3-(2,2,2-trifluoroethoxymethyl)-3-methyloxetane and 3-(2,2,3,3,4,4,4-heptafluorobutoxymethyl)-3-methyloxetane (Poly 3/7 FOX, 25:75) by Procedure A as in Example C1 and using TMP as a cross-linking agent.

A 25 mL, 3-necked flask was dried with a heat gun under nitrogen and charged with the title co-prepolymer (5.007 g, 1.35 meq), TMP (208 mg, 4.66 meq), IPDI (682 mg, 6.12 meq), and dibutyltin dilaurate (6 mg, 0.1% wt.). The contents were mixed and casted into a Teflon mold. The mixture was then degassed, placed in an oven, and cured at 65°C for 16 h. The cured material was removed from the mold and characterized as follows:

15	Nature:	Tack-free Elastomer
	Color:	Opaque
	Static Contact Angle (H ₂ O)	114°
	Surface Energy	15.4 ergs/cm ²
	Mechanical Properties	
20	- Tensile Modulus	34 psi
	- Elongation at Break	1256%
	- Tensile Strength	427 psi
	Hardness	5 Shore A
	Glass Transition Temperature, DSC	-42°C
25	Water Absorption	
	- 9 days/25°C	0.22% by Weight Gain
	- 16 h/100°C	0.25% by Weight Gain
	Chemical Resistance	
30	- Stable	Methanol, Hexane, Toluene, 20% Sodium hydroxide, and DMF
	- Swell	THF and Freon 113

EXAMPLE C4

Preparation of Poly 3-FOX/Des-W/Isonol Polyurethane Elastomer

This example illustrates the preparation of polyurethane elastomer from the homo-prepolymer of 3-(2,2,2-trifluoroethoxymethyl)-3-methyloxetane (Poly 3-FOX) by Procedure A. This Example is the same as in Example C1 except that Example C1 uses the 7-FOX.

Note that although the resulting 3-FOX polyurethane elastomer contains only 29% fluorine as compared to Teflon which has 76% fluorine, the contact angle is the same as Teflon. Further, the polyurethane elastomer of this invention is clear, making it useful for optical applications.

A 10 mL round bottomed flask was dried under nitrogen and charged with Poly 3 FOX (5.003 g, 1.25 meq), Isonol 93 (26 mg, 0.29 meq), Des-W (214 mg, 98%, 1.59 meq), and dibutyltin dilaurate (8 mg). The contents were mixed and casted into a Teflon mold. The mixture was then degassed, placed in an oven, and cured at 65°C for 8 h. The cured material was removed from the mold and characterized as follows:

Nature:	Tack-free Elastomer
Color	Clear, transparent
Static Contact Angle (H ₂ O)	110°
Mechanical Properties	
- Tensile Modulus	79 psi
- Elongation at Break	926%
- Tensile Strength	670 psi
Hardness	11 Shore A
Glass Transition Temperature, DSC	-40°C
Chemical Resistance	
- Stable	Methanol, hexane, toluene, 20% Sodium hydroxide & DMF
- Swell	Freon 113

EXAMPLE C5

Preparation of Poly 3/15-FOX/Des-W/Isonol Polyurethane Elastomer

This example illustrates the preparation of polyurethane elastomer from a 25:75 Co-prepolymer of 3-(2,2,2-trifluoroethoxymethyl)-3-methyloxetane and 3-(2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-pentadecafluorooctyloxymethyl)-3-methyloxetane (Poly 3/15 FOX, 25:75) by Procedure A.

Note that this Example shows that long side-chains on the prepolymers of this invention do not sterically inhibit polymerization. Additionally, the contact angle has increased significantly as a result of the presence of the long side-chains.

A 50 mL, 3-necked flask was dried with a heat gun under nitrogen and charged with the poly 3/15-FOX (11.003 g, 3.67 meq), Isonol 93 (74 mg, 0.83 meq), Des-W (607 mg, 98.5% pure, 4.53 meq), and dibutyltin dilaurate (5.2 mg). The contents were mixed and casted into a Teflon mold. The mixture was then degassed, placed in an oven, and cured at 65°C for 36 h. The cured material was removed from the mold and characterized as follows:

Nature:	Tack-free Elastomer
Color	Opaque
Static Contact Angle (H ₂ O)	128°
Mechanical Properties	
- Tensile Modulus	67 psi
- Elongation at Break	1117%
- Tensile Strength	344 psi
Hardness	5 Shore A
Glass Transition Temperature, DSC	-47°C
Water Absorption	
- 9 days/25°C	0.20% by Weight Gain
- 16 h/100°C	0.22% by Weight Gain
Chemical Resistance	
- Stable	Methanol, hexane, toluene, 20% sodium hydroxide,

carbon tetrachloride,
ethanol, DMSO, non-leaded
gasoline, acetic acid, 3 N
sulfuric acid, & DMF
THF, MTBE and Freon 113

5 - Swell

EXAMPLE C6

Preparation of Poly 3/13-FOX/Des-W/Isonol Polyurethane Elastomer

10 This example illustrates the preparation of polyurethane
from a 50:50 Co-prepolymer of 3-(2,2,3,3,4,4,4-
heptafluorobutoxymethyl)-3-methyloxetane and 3-
15 (3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyloxymethyl)-3-
methyloxetane (Poly 3/13 FOX, 50:50) by Procedure A.

20 A 25 mL round bottom flask was dried with a heat gun under
nitrogen and charged with the poly 3/13-FOX (2.36 g, 0.89 meq),
Isonol 93 (18 mg, 0.20 meq), Des-W (149 mg, 98.5% pure, 1.11 meq),
and dibutyltin dilaurate (5.2 mg). The contents were mixed and
casted into a Teflon mold. The mixture was then degassed, placed
in an oven, and cured at 75°C for 18 h. The polymer sample was
removed from the mold and characterized as follows:

25 Nature:	Tack-free Elastomer
Color	Opaque
Contact Angle (H ₂ O):	126°

EXAMPLE C7

Preparation of Poly 3/13/17/21-FOX/N-100 Polyurethane Elastomer

30 This example illustrates the preparation of polyurethane from a
co-prepolymer of 3-(3,3,4,4,5,5,6,6,7,7,8,8,8-
tridecafluorooctyloxymethyl)-3-methyloxetane, 3-
35 (3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-
Heptadecafluorodecyloxymethyl)-3-methyloxetane, and 3-

(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,12,12,12-Heneicosafuorododecyloxymethyl)-3-methyloxetane (Poly 3/R FOX) by Procedure A. No alcohol or amino-based cross-linking agent was used. N-100 is a polyisocyanate.

5 This Example represents the first time a terpolymer using commercially available alcohols is incorporated into a polymer matrix. Note the extremely high contact angle of 135° indicating very low surface energy and high hydrophobicity.

10 A 10 mL beaker was charged with the title terpolymer (2.003 g, 0.80 meq), N-100 (151 mg, 0.79 meq), and dibutyltin dilaurate (5.2 mg). The contents were mixed and casted into a Teflon mold. The mixture was then degassed, placed in an oven, and cured at 65°C for 23 h. The cured material was an opaque, tack-free elastomer, that
15 exhibited a contact angle of 135° with doubly distilled water.

EXAMPLE C8

Preparation of Poly 15-FOX/N-3200 Polyurethane Elastomer

20 This example illustrates the preparation of polyurethane from the homo-prepolymer of 3-(2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-pentadecafluorooctyloxymethyl)-3-methyloxetane (Poly 15-FOX) by Procedure A. No cross-linking agent was used. N-3200 is a polyisocyanate.

25 This Example provides guidance in coating a substrate to produce a thin, continuous film, polyurethane coating. Note the extremely high contact angle of 145°.

30 A 10 mL beaker was charged with the title copolymer (3.200 g, 1.07 meq), N-3200 (212 mg, 1.17 meq), and dibutyltin dilaurate (3 mg). The contents were mixed, degassed, and spread on an aluminum plate (2" x 0.5") with a Doctor's blade to the desired thickness of between 10 to 20 mils. The plate was placed in an oven and cured at 75 °C for 16 hours. The cured coating was tack-free, opaque and
35 exhibited a contact angle of 145° with doubly distilled water. The

contact angle of the title elastomer is compared with the contact angle of Teflon in Fig. 1.

D. FOX/THF CO-PREPOLYMERS and POLYURETHANES

Prepolymers composed of fluorinated polyether segments and hydrocarbon THF segments may be cured with di- and poly-isocyanates to produce fluorinated elastomers having exceptional hydrophobicity and good physical and mechanical properties.

The following provide by way of example the methods used to synthesize the FOX/THF coprepolymers and the synthesis of the polyurethanes of this invention. Examples D1-D5 are directed to the FOX/THF coprepolymer synthesis and Examples D6-D9 are directed to the synthesis of the FOX/THF polyurethane elastomers.

EXPERIMENTAL

^1H , ^{13}C , and ^{19}F NMR analyses were conducted on a 300 MHz, Bruker MSL-300 spectrometer. The proton and carbon chemical shifts are recorded in ppm downfield from tetramethylsilane. Fluorine shifts are reported in ppm relative to trichlorofluoromethane. Infrared analyses were conducted on a Nicolet SX 5 spectrometer. Gel Permeation Chromatography was conducted on a Waters gel permeation chromatograph equipped with four ultrastyrigel columns (100 Å, 500 Å, 1000 Å, and 10,000 Å), a refractive index detector, and a Datamodule 730. THF was used as the mobile phase. The GPC was calibrated with a set of well-characterized (i.e., M_n , M_w are well known) polystyrene standards (Narrow Standards), and thus the number average molecular weight (M_n) and weight average molecular weight (M_w) are reported relative to polystyrene. Mechanical properties were measured with a Model 1122 Instron, and dynamic mechanical properties were measured with Model 660 Rheometrics Mechanical Spectrometer (RMS). Static contact angles of water with polymer surfaces were measured with a Goniometer using doubly distilled water. Differential scanning calorimetry (DSC) and

thermogravimetric analysis (TGA), were performed on a DuPont 990 thermal analyzer system. DSC measurements were made at a heating rate of 10°C/min in air, whereas TGA measurements were made at a heating rate of 20°C/min in air at a flow rate of 20 mL/min.

5 Surface energy was measured by the method of Wu et al. Inherent viscosity was measured in THF at a concentration of 0.50 g/dL at 25 °C.

10 Solvents were purchased from Aldrich Chemical Co., and used without purification. Tetrahydrofuran was purified by distillation prior to polymerization. Isocyanates such as Isophorone diisocyanate (IPDI), saturated methylene-diphenyldiisocyanate (Des-W), hexamethylene diisocyanate (HDI), and N-3200 (biuret of HDI) were obtained from Mobay Chemical Co.,
15 and used without further purification. Jeffamines were obtained from Texaco Oil Co., whereas heptafluorobutan-1-ol was purchased from Aldrich Chemical Co. BF₃·THF was prepared from BF₃ etherate and tetrahydrofuran, and was distilled prior to use.

20 EXAMPLE D1

Preparation of 7-FOX/THF Co-prepolymer in 60:40 Ratio

25 This example illustrates the synthesis of a 60:40 co-prepolymer of 3-heptafluorobutoxymethyl-3-methyloxetane and Tetrahydrofuran (Poly 7-FOX/THF 60:40).

Note that no solvent is used in the preparation of the co-prepolymer.

30 A 500 mL, 4 necked flask fitted with a mechanical stirrer, condenser, thermometer, and a nitrogen inlet/outlet was charged with freshly distilled THF (27.0 g, 0.375 moles), butane-1,4-diol (0.50 g, 5.56 mmoles), and BF₃·THF (1.90 g, 13.6 mmoles). The mixture was cooled to 8 °C, and 3-heptafluorobutoxy-methyl-3-

methyloxetane (7-FOX, 70.0 g, 0.246 moles) was added, dropwise, over 1.5 h. The temperature was maintained below 12°C, and the progress of the reaction was monitored by ¹H NMR. The mixture was stirred at room temperature for 2 h and then quenched with water (100 mL). The reaction mixture was diluted with methylene chloride (100 mL) and the organic layer was washed with water (200 mL), 10% aqueous sodium bicarbonate solution (2 x 200 mL), water (200 mL), and brine (200 mL). The mixture was then slowly precipitated into 1.5 L of methanol, and the polymer layer was dissolved in methylene chloride (200 mL), dried (MgSO₄), filtered, and concentrated on a rotary evaporator to give 107 g (83%) of the title co-prepolymer, an opaque, colorless oil. GPC analysis revealed that the co-prepolymer was devoid of cyclic oligomers. The co-prepolymer was characterized as follows: ¹H NMR (CDCl₃/F113) δ: 3.87 (t, J = 13.4 Hz), 3.46 - 3.22 (m, backbone protons), 1.61 (br s), and 0.93 (s, -CH₃). (The ratio of 7-FOX units to THF units, as determined by ¹H NMR analysis, was 63:37); Equivalent Weight based on TFAA end group analysis by ¹H NMR = 6,230; Equivalent Weight by p-toluenesulfonyl isocyanate/dibutyl amine titration = 5,890; ¹³C NMR δ: 17.13, 25.56, 26.71, 41.24, 41.40, 41.55, 68.45 (t), 70.75, 71.38, 73.29, 73.93, and 75.75 (signals from carbons bearing fluorine are not included); ¹⁹F NMR δ: -81.2 (3 F), -121.0 (2 F), and -127.7 (2 F); GPC: M_n = 13,363, M_w = 25,526, Polydispersity = 1.91; Inherent Viscosity = 0.125 dL/g; DSC: T_g = -43°C.

EXAMPLE D2

Preparation of 7-FOX/THF Co-prepolymer in 90:10 Ratio

This example illustrates the synthesis of a 90:10 co-prepolymer of 3-Heptafluorobutoxymethyl-3-Methyloxetane and Tetrahydrofuran (Poly 7-FOX/THF 90:10).

A 50 mL, 3 necked flask fitted with a mechanical stirrer,

condenser, thermometer, and a nitrogen inlet/outlet was charged with methylene chloride (9 mL), 1,4 butanediol (62 mg, 0.69 mmole), and BF₃·THF (260 mg, 1.86 mmole). After stirring at room temperature for 30 minutes, the mixture was heated to reflux for 5 minutes and then cooled to 8°C. Next, a solution of 3-heptafluorobutoxymethyl-3-methyloxetane (7-FOX, 10.2 g, 35.9 mmole) in Freon 113 (3 mL) was added over a period of 15 minutes. The resulting mixture was stirred at room temperature for 1 h, diluted with methylene chloride (20 mL) and Freon 113 (10 mL), and quenched with water. The organic layer was washed with 10% aqueous sodium bicarbonate solution (50 mL), water (50 mL), and brine (50 mL), dried (MgSO₄), filtered, and concentrated on a rotary evaporator to give 10.3 g (96.3 %) of the title co-prepolymer, a clear, colorless oil. GPC analysis indicated that the co-prepolymer was contaminated with ca. 1.3% of cyclic tetramer. The co-prepolymer was characterized as follows: ¹H NMR (CDCl₃/F113) δ 0.95 (s), 1.64 (broad), 3.25 - 3.37 (m), 3.48 (s), and 3.89 (t, J = 13.60 Hz) (The ratio of 7-FOX units to THF units, as determined by ¹H NMR analysis, was 90:10); Equivalent weight based on TFAA end group analysis by ¹H NMR = 6,649; ¹³C NMR (CDCl₃/F113) δ 17.08, 26.54, 26.69, 41.25, 41.41, 41.57, 41.81, 68.49 (t), 70.73, 71.39, 73.30, 73.52, 74.00, and 75.79 (signals from carbon bearing fluorines are not included due to complex splitting patterns and low peak intensities); GPC: M_n = 11,586, M_w = 23,991, Polydispersity = 2.07; DSC, T_g = -41 °C.

EXAMPLE D3

Preparation of 7-FOX/THF Co-prepolymer in 35:65 Ratio

This example illustrates the synthesis of a 35:65 co-prepolymer of 3-Heptafluorobutoxymethyl-3-methyloxetane and Tetrahydrofuran (Poly 7-FOX/THF 35:65).

Note that no solvent is used in this Example and that no cyclic tetramer was detected.

A 100 mL round bottomed flask fitted with a reflux condenser,
5 nitrogen inlet/ outlet, thermometer and an addition funnel was
charged with freshly distilled THF (25 mL, 22.2 g, 308 mmol), BF₃,
THF (366 mg, 2.6 mmol), and 1,4-butanediol (90 mg, 1.0 mmol). The
mixture was stirred at room temperature for 10 mins, cooled to 10°C
and treated, dropwise, with 3-heptafluorobutoxymethyl-3-
10 methyloxetane (7-FOX, 10.2 g, 35.9 mmol) over a period of 10 mins.
The mixture was stirred at 10°C for 10 mins and then at room
temperature for 2 days. The progress of the reaction was monitored
by ¹H NMR. The reaction mixture was diluted with methylene
chloride and Freon 113 (60:40), and then quenched with water (10
15 mL). The organic layer was separated and washed with water (30
mL), 10% aqueous sodium bicarbonate solution (30 mL), water (30 mL)
and brine (30 mL). The organic layer was dried (MgSO₄), filtered,
and concentrated under reduced pressure to give 16.2 g of the title
co-prepolymer, a colorless, viscous oil. GPC analysis indicated
20 that the co-prepolymer was devoid of cyclic oligomers. The co-
prepolymer was characterized as follows: ¹H NMR (CDCl₃) δ 0.95 (s),
1.63-1.64 (br s), 3.24 (s), 3.42-3.48 (m), and 3.87 (t) (The ratio
of 7-FOX units to THF units by ¹H NMR was 66:34); Equivalent weight
based on TFAA end group analysis by ¹H NMR = 6,104; ¹³C NMR 17.32,
25 26.93, 27.08, 41.59, 41.76, 41.95, 68.89 (t), 70.88, 71.67, 73.65,
74.34, 74.39, 76.22, and 76.57 (signals from carbon bearing
fluorines are not included due to complex splitting patterns and
low peak intensities); GPC: M_n = 12,576, M_w = 20,018, and
Polydispersity = 1.59.

EXAMPLE D4

Preparation of 13-FOX/THF Co-prepolymer in 50:50 Ratio

This example illustrates the synthesis of a 50:50 co-prepolymer of 3-(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyloxymethyl)-3-methyloxetane and Tetrahydrofuran (Poly 13-FOX/THF 50:50).

This is another example of a FOX/THF co-prepolymer with the FOX monomers having long fluorinated side-chains. As in the previous Example C5, the presence of the long side-chains unexpectedly do not hinder the polymerization. Further, unlike the polymerization of the bis-monomers, no cyclic tetramers were detected. No solvent was used in this polymerization.

A 250 mL, 3-necked, round-bottom flask fitted with a condenser, a thermometer, a nitrogen inlet/outlet, and an addition funnel was charged with freshly distilled tetrahydrofuran (36 g, 0.5 mol), 1,4-butanediol (68 mg, 0.75 mmol), and boron trifluoride tetrahydrofuranate (250 mg, 1.786 mmol). The solution was cooled to 10°C and 3-(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyloxymethyl)-3-methyloxetane (13-FOX, 35.3 g, 78.8 mmol) was added over a period of 45 mins. The mixture was stirred at 10°C for 3 h and then at room temperature for 16 h. ¹H NMR of an aliquot revealed that the reaction of ca. 90% complete. The reaction mixture was then heated at reflux for 2 h, at which point NMR analysis indicated >95% completion. Water was added and the organic layer was slowly precipitated into methanol. The precipitated material was dissolved in 1:1 Freon 113/methylene chloride, dried (MgSO₄), filtered, and concentrated on a rotary evaporator to give 36.5 g (89%) of the title prepolymer, a viscous oil. GPC analysis of the prepolymer revealed total absence of cyclic oligomers. The prepolymer was characterized as follows: ¹H NMR 3.67 (t), 3.42 (br s), 3.32-3.21 (m), 2.36 (tt), 1.63 (br s), and 0.93 (s). (The ratio of 13-FOX units to THF units by ¹H NMR was 50:50); Equivalent weight based on TFAA end group analysis by ¹H NMR = 8,903; GPC: Mn = 25,244, Mw = 35,968, Polydispersity = 1.43; ¹³C NMR 17.53, 26.95, 27.07, 32.07 (t), 41.30, 41.50, 41.71, 63.55, 71.0, 71.62, 71.89, 73.88, 74.41, and 75.35 (signals from carbon

bearing fluorines are not included due to complex splitting patterns and low peak intensities).

EXAMPLE D5

Preparation of 15-FOX/THF Co-prepolymer in 60:40 Ratio

This example illustrates the synthesis of a 60:40 co-prepolymer of 3-(2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-pentadecafluorooctyloxymethyl)-3-methyloxetane and Tetrahydrofuran (Poly 15-FOX/THF 60:40).

This is another example of a FOX/THF co-prepolymer with the FOX monomers having long fluorinated side-chains. As in the previous Examples C5 and D4, the presence of the long side-chains unexpectedly do not hinder the polymerization. Further, unlike the polymerization of the bis-monomers, no cyclic tetramers were detected.

No solvent was used in this polymerization.

A 200 mL, 3-necked round bottomed flask fitted with a reflux condenser, nitrogen inlet/outlet, a magnetic stirring bar, a thermometer and an addition funnel was charged with anhydrous THF (18.14 g, 0.25 mol), 1,4-butanediol (25.7 mg, 0.29 mmol), and boron trifluoride tetrahydrofuranate (100 mg, 0.71 mmol). The mixture was cooled to 5°C and 3-(2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-pentadecafluorooctyloxymethyl)-3-methyloxetane (15-FOX, 20.0 g, 41.3 mmol) was added over a period of 10 mins. The mixture was stirred at room temperature for 2 days, quenched with water (2 mL), and slowly precipitated into methanol. The precipitated material was dissolved in a 1:1 mixture of methylene chloride and Freon 113, dried, filtered and concentrated on a rotary evaporator to give 17.3 g of the title co-prepolymer, a viscous, colorless oil. The ratio of the 15-FOX units to THF units, as determined by ¹H NMR analysis, was 59:41. The co-prepolymer was characterized as follows: ¹H NMR δ 3.89 (t, 13.5 Hz), 3.48-3.41 (m), 3.24 (s), 1.63 (s), and 0.95 (s); Equivalent Weight based on TFAA end group

analysis by ^1H NMR = 9,321; ^{13}C NMR δ 17.27, 26.86, 27.02, 41.51, 41.68, 41.85, 69.01 (t), 70.94, 71.57, 73.55, 74.18, and 76.09.

Polyurethanes from FOX/THF Co-prepolymers

EXAMPLE D6

Preparation of Poly 7-FOX/THF Based Polyurethane

This example illustrates the preparation of a polyurethane from Poly 60:40 7-FOX/THF and Des-W. Note that although the incorporation of THF into the prepolymer backbone results in 40% less fluorine than in a 7-FOX prepolymer (no THF), the contact angle and T_g of the 7-FOX/THF polyurethane is comparable to the polyurethane derived from the 7-FOX prepolymer.

A 50 mL, 3-necked flask was dried with a heat gun under nitrogen and charged with poly 60:40 7-FOX/THF (11.00 g, 3.16 meq), Isoh93 (64 mg, 0.73 meq), Des-W (524 mg, 3.89 meq), and dibutyltin dilaurate (5 mg). The contents were mixed, casted into a Teflon mold, and degassed under reduced pressure for 15 mins. The mixture was then cured in an oven, under nitrogen, at 65°C for 16 h. The cured material was removed from the mold and characterized as follows:

Nature:	Opaque, Tack-free Elastomer
Contact Angle (H_2O)	117°
Surface Energy	13.5 ergs/cm ²
Mechanical Properties	
Tensile Modulus	53 psi
Elongation at Break	1624%
Tensile Strength	624 psi
Glass Transition Temperature, DSC	-43°C
Peel Strength, EPDM Rubber Substrate	>10 lb/in, Cohesive Failure

Example D7
Preparation of a Coating From Poly 7-FOX/THF Polyurethane

This Example is the same as Example D6, except that it teaches the process for coating a substrate with a thin film of fluorinated polyurethane prepared from poly-7-FOX/THF (60:40), Des-W and Isonol 93.

A 50 ml, 3-necked flask was dried with a heat gun under nitrogen and charged with poly7-FOX/THF (60:40, 11.0 g, 3.16 meq), Des-W (524 mg, 3.89 meq), Isonol 93 (64 mg, 0.73 meq) and dibutyltin dilaurate (5 mg). The contents were mixed, diluted with anhydrous THF (10 ml) and spread on a stainless steel substrate with a Doctor's blade. Alternately, the substrate can be dipped, or spray coated with the above formulation. The coated substrate was dried in a hood for 4 hours and then heated in an oven at 40 °C for 2 hours and then at 65 °C for 16 hours. The cured coating was a continuous, tack-free film, and exhibited a contact angle of 118° with doubly distilled water.

EXAMPLE D8
Preparation of Poly 7-FOX/THF Polyurethane in 35:65 Ratio

This example illustrates the preparation of a polyurethane from Poly 35:65 7-FOX/THF, Des-W and Isonol 93.

In a manner similar to that described in Example D6, a mixture of poly 35:65 7-FOX/THF (10.02 g, 2.50 meq), Isonol 93 (53 mg, 0.60 m eq), Des-W (417mg, 98% pure, 3.10 meq), and dibutyltin dilaurate (1 drop) was cured in a Teflon mold at 65°C for 16 h. The cured material was removed from the mold and characterized as follows:

Nature:	Translucent, Tack-free Elastomer
Contact Angle (H ₂ O)	108°
Mechanical Properties	

Tensile Modulus	205 psi
Elongation at Break	420%
Tensile Strength	571 psi
Glass Transition Temperature, DSC	-41°C

5

EXAMPLE D9

Preparation of Poly 15-FOX/THF Polyurethane

10 This example illustrates the preparation of a polyurethane from Poly 60:40 15-FOX/THF and N-3200. Note that the contact angle of the resulting polyurethane was very high (126 °) despite dilution of the polymer with the THF segments. Further, there was no change in T_g . In comparison, the non-diluted 15-FOX polyurethane of Example C8 exhibited the highest contact angle ever observed of 145°.

15

In a manner similar to that described in Example D6, a mixture of poly 60:40 15-FOX/THF (3.0 g, 0.73 meq), N-3200 (135 mg, 0.73 meq), THF (0.5 mL), and dibutyltin dilaurate (3 mg) , were cured in a Teflon mold, under nitrogen, at 75°C for 3 days. The cured material was an opaque, tack free elastomer, with following properties: T_g (DSC) = -46°C; Contact Angle with Water = 126°.

20

EXAMPLE D10

Preparation of Poly 13-FOX/THF Polyurethane

25

This example illustrates the preparation of a polyurethane from Poly 50:50 13-FOX/THF and Des-W

30 In a manner similar to that described in Example D6, a mixture of poly 50:50 13-FOX/THF (5.002 g, 1.50 meq), Isonol 93 (5.3 mg, 0.06 meq), Des-W (210 mg, 98% pure, 1.56 meq), and dibutyltin dilaurate (4 mg) was cured at 65°C for 2 days. The cured material was an opaque, tack free elastomer with following properties: T_g

(DSC) = -43°C; Contact Angle with Water = 123°C; Mechanical Properties: Tensile Modulus = 35 psi, Elongation at Break = 972%, Tensile Strength = 487 psi.

5

10

It should be understood that various modifications within the scope of this invention can be made by one of ordinary skill in the art without departing from the spirit thereof. We therefore wish our invention to be defined by the scope of the appended claims as broadly as the prior art will permit, and in view of the specification if need be.